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Sound velocity and attenuation measurements of perfluorocarbon liquids using photoacoustic methods

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Abstract— **A method to measure the phase velocity and attenuation of liquids over a frequency range of 100-1000 MHz using a photoacoustic method is presented. A pulsed laser directed at a thin gold or ink layer was used to create a broadband ultrasonic wave and was used as the source. An ultrasound transducer (375 or 750 MHz center frequency) positioned above the source was used as the receiver. The phase and amplitude spectra of signals transmitted through a liquid between the photoacoustic source and ultrasound receiver were used to determine the phase velocity and attenuation as a function of frequency. The method was first validated using water, ethanol and castor oil. The phase velocity and attenuation were similar to published values. Water and ethanol showed no dispersion with frequency, while castor oil increased from 1508 m/s at 200 MHz to 1561 m/s at 700 MHz. Three perfluorocarbon (PFC) liquids (perfluorohexane, perfluoroheptane and FC-77) were then measured. The phase velocity was 480, 516 and 557 m/s at 200 MHz for perfluorohexane, perfluoroheptane and FC-77, respectively, and increased by approximately 1.5% at 700 MHz. The attenuation was similar for all three PFC liquids at $0.352f^{1.56}$ dB/cm/MHz^{n}.**

I. INTRODUCTION

Several methods exist for measuring the speed of sound and attenuation of solids and liquids using ultrasound. An insertion method can be used, where the signal between two transducers is measured with and without the sample. However knowledge of the coupling fluid sound speed and attenuation is required. Alternatively, a variable path-length method can be used, which does not require a separate reference measurement with water but relies on changes to the signal as the distance between two transducers is varied. An excellent review of different methods can be found in [1].

While extensive data have been published on the speed of sound and attenuation of liquids, tissue and solids over various frequency ranges, studies using frequencies over 100 MHz are less common. Highly attenuating liquids are difficult to measure at high frequencies, and equipment must be precisely positioned for accurate measurements. There are substantial published data on dispersion and attenuation measurements of liquids and tissue over frequency ranges typically used in clinical studies (1-15 MHz), where dispersion is negligible or very small. However as high frequency ultrasonic and photoacoustic imaging (20-60 MHz) become increasingly popular, knowledge of how the phase velocity and attenuation of liquids and tissue vary with frequency become important to create spatially-accurate images or be used in quantitative measurements. Additionally, acoustic and photoacoustic simulations and models frequently assume constant sound speed over the frequency range used. Since the phase velocity and attenuation are dependent on each other, the Kramers-Kronig relations can be used to extrapolate the phase velocity to lower frequencies outside the range of this study [2].

Photoacoustics is the generation of ultrasonic pressure waves when laser energy is absorbed by a material. As an alternative to using two co-aligned transducers to measure the sound speed and attenuation through a liquid, a photoacoustic source could be used as the transmit transducer. A thin gold or carbon layer irradiated with a pulsed laser would create a pressure wave that can be detected using a standard ultrasound transducer. The photoacoustic pressure wave from a thin layer would have a broad spectrum, wider than typical piezoelectric transducers used today. The photoacoustic method has been used to measure the sound speed and attenuation of liquids up to 100 MHz [3], however due to the difficulty in measuring highly attenuation materials, their measurement of castor oil was only possibly up to 30 MHz.

We describe the development of an ultrahigh frequency (UHF) photoacoustic method to measure the phase velocity and attenuation of highly attenuating liquids from 100-1000 MHz, requiring only small quantities of liquid (20 μL). This allows for the measurement of rare or expensive liquids which could not be used in a typical ultrasonic device.

II. THEORY

The phase velocity and attenuation of a liquid can be determined by measuring the photoacoustic signal at two different transducer positions above the sample, d_1 and d_2. A Fourier transform is used to determine the phase spectrum $\varphi(f)$ and amplitude spectrum $A(f)$ at each position. Following [4], the phase velocity can be calculated using

$$c(f) = \frac{2\pi f \Delta d}{\varphi_2(f) - \varphi_1(f)}, \qquad (1)$$

Where $\Delta d = d_2 - d_1$ is the distance between transducer positions, and $\varphi_2(f)$ and $\varphi_1(f)$ are the phase spectra at the two transducer positions. The attenuation (dB/cm) can be calculated using

$$\alpha(f) = \frac{8.686}{\Delta d}\ln\left(\frac{A_1(f)}{A_2(f)}\right), \tag{2}$$

where $A(f)$ is the signal amplitude [5]. The factor 8.686 was used to convert from Np to dB. A power law fit of the form

$$\alpha(f) = \alpha_1 + \alpha_0 f^n \tag{3}$$

was used to fit the attenuation vs. frequency data, where α_0 is the attenuation coefficient and n is exponent in the power law [2]. The power n is typically close to 2 for liquids and 1 for tissue.

III. MATERIALS AND METHODS

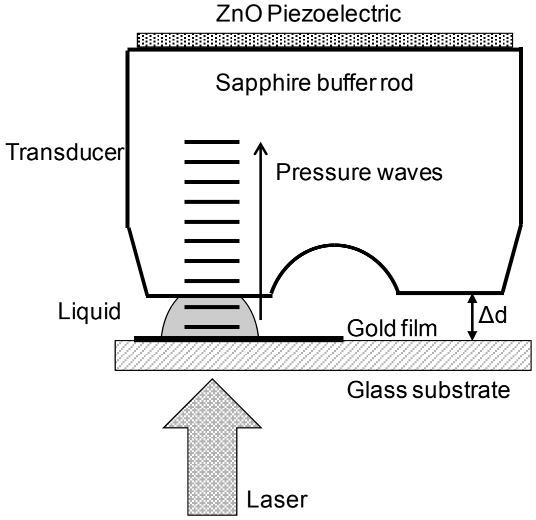
A. *Photoacoustic Microscope*

A SASAM 1000 photoacoustic microscope (Kibero GmbH Germany) was used for all measurements. It consists of an Olympus IX81 inverted optical microscope (Olympus, Japan) with a transducer positioned above the sample holder. A 532 nm laser (Teem Photonics, France) was collimated into the optical path and focused to a 5 μm spot diameter using a 4x optical objective. The optical view allowed for precise positioning of the transducer and laser. A linear screw precision stage was used to move the transducer in the z-direction (away from the sample) with a resolution of 0.01 μm (Physik Instrumente GmbH, Germany). The entire system was contained in a constant temperature environment of 36ºC. Specific details of the system construction can be found elsewhere [6][7].

The laser power output was measured from the collimator and was adjustable to a maximum of 1.0 uJ per pulse. The laser had a pulse width of 330 ps with a repetition frequency of up to 4 kHz. Photoacoustic signals were detected using a 375 MHz transducer (60° aperture angle) and a 750 MHz transducer (100º aperture angle) each with a -6 dB bandwidth of approximately 45%. The bandwidth was measured using pulse echo measurements from a glass substrate, however the usable bandwidth extended greater than described and depended on the coupling fluid used. The signal was amplified by a low noise 40 dB amplifier (Miteq, USA) and digitized at a rate of 8 GHz (Acqiris, USA).

B. *Measurements*

A glass substrate with a 200 nm thick gold layer or ink layer was placed in the sample holder. A drop of the liquid to be measured was deposited onto the layer. The laser spot was then focused onto the layer, and the rim of the transducer was positioned approximately 50 μm above laser spot, ensuring contact was made with the liquid (figure 1). The transducer rim was used as a flat receiver was required to measure the signal as a function of transducer position, as the signal variations were too large using the focused cavity. The signal was recorded as the transducer was moved away from the layer using a 1 μm step size for a total distance travelled of 50 μm. 200-1000 signals were averaged at each step. The entire measurement took approximately 15 seconds. For the attenuation measurements, a zero-padded FFT was performed on the signal at each step, resulting in 50 spectra over the entire measurement. The spectra at two different locations were used in equation 2 to determine the attenuation, where the distance was known from the step size. Generally 10 attenuation calculations were averaged while ensuring Δd was greater than 20 μm. For phase velocity measurements, the signal was rotated so the centroid of the signal was at the beginning [8], then the FFT was calculated. The phase was unwrapped and a linear fit was applied to the phase to determine the y-intercept. The phase was then shifted as described in [9] to correct the phase unwrapping algorithm. The phase at two different locations along with Δd was used in equation 1 to determine the phase velocity. As with the attenuation calculations, approximately 10 calculations were averaged for the final value. Measurements were made using two transducers with center frequencies of 375 and 750 MHz and superimposed onto the same graph.



C. *Coupling Fluids*

The phase velocity and attenuation of six different liquids were determined. Three liquids that have been studied extensively were used to verify the method: water, ethanol and castor oil which have a range of sound speeds and viscosities. Three perfluorocarbon liquids were then measured: perfluorohexane (C_6F_{14}), perfluoroheptane (C_7F_{16}) and FC-77, a mixture of perfluorooctanes (C_8F_{18} and $C_8F_{18}O$). A summary of the liquids and their properties used in these experiments, along with the published sound speed and attenuation values is shown in table I. Due to the small distance between the transducer and photoacoustic layer, small liquid volumes could be used, as little as 20 μL. However to use such small volumes, the liquid required either high surface tension (such as water) or high viscosity (such as oil) to maintain a round shape and contact with the transducer during measurements. Liquids with high vapor pressures, such as alcohols and PFCs required increased volume to maintain acoustic contact between the transducer and photoacoustic layer.

IV. RESULTS AND DISCUSSION

A. Method Verification

The method was verified using water, ethanol and castor oil. These three liquids were chosen as water and ethanol have different sound velocities (1520 and 1120 m/s, respectively) but similar attenuation, while castor oil has a similar sound velocity to water, but a much higher attenuation. Additionally, water and ethanol have negligible dispersion with $n = 2$, while castor oil is known to exhibit dispersion. The phase velocity and attenuation over a 100-1000 MHz frequency range are shown in figure 1a-b. The results are summarized in table I.

For water, the measured sound speed was 1520 m/s, and the attenuation was $0.0022f^{1.98}$ dB/cm/MHz^n, close to the published values of 1522 m/s [10] and $0.0014f^2$ dB/cm/MHz^2 [11]. For ethanol, the measured speed of sound was 1142 m/s, and the

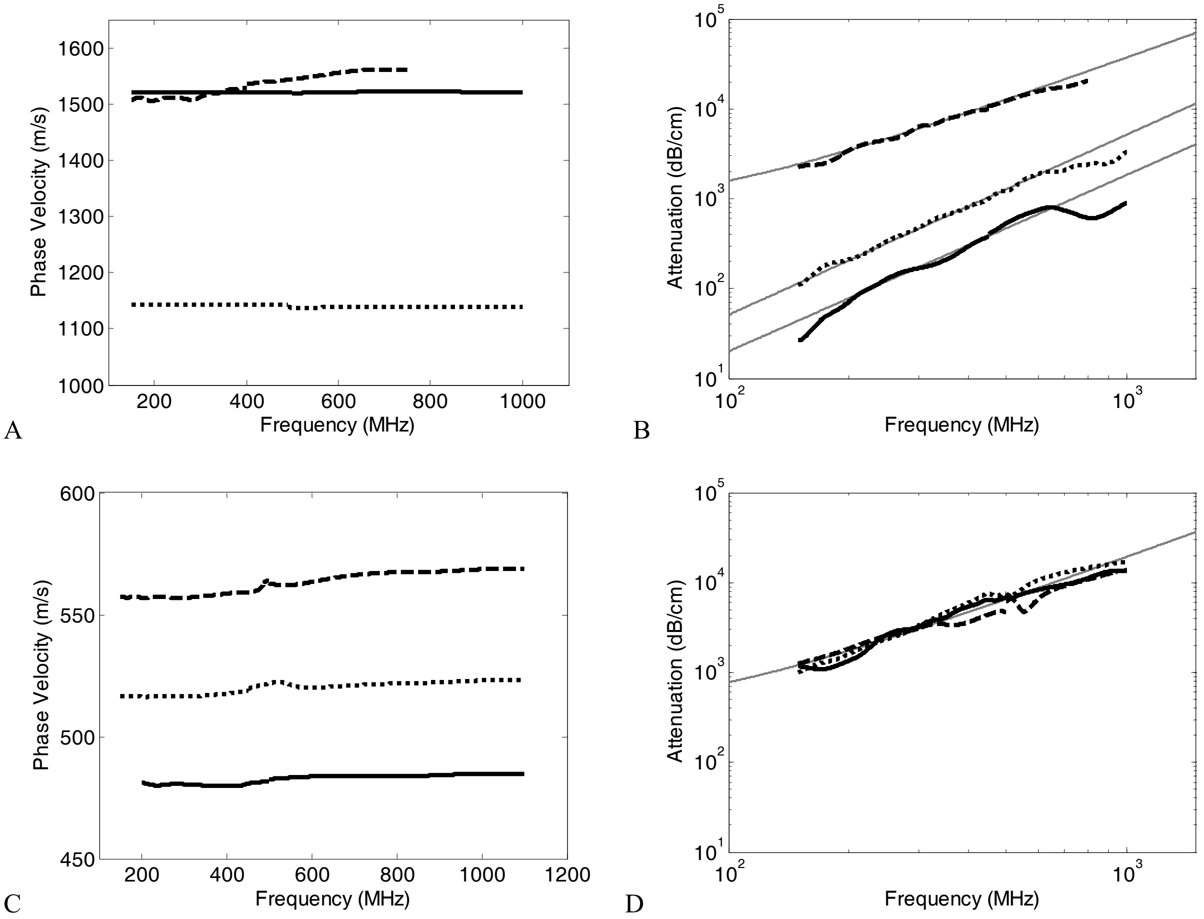


Figure 2. The phase velocity and attenuation of water (solid line), ethanol (dotted line) and castor oil (dashed line), are shown in (a) and (b), respectively. The phase velocity and attenuation of perfluorohexane (solid line), perfluoroheptane (dotted line) and FC-77 (dashed line) are shown in (c) and (d), respectively. The measurements from the 375 and 750 MHz transducers were superimposed onto the same graph. The gray solid line indicates the line of best fit using equation 3 and is given in table I. The three PFC attenuation spectra were combined to determine the line of best fit.

TABLE I. PROPERTIES OF LIQUIDS

Liquid	Structure	Boiling Point (°C)	Density @ 36°C (kg/m^3)	Published Sound speed (m/s) 20 MHz	Change in sound speed 200-700 MHz	Published Attenuation (dB/cm/MHz^n)	Measured Attenuation (dB/cm/MHz^n)
Water	H_2O	100	994	1521.7	1521	$0.0014\ f^2$	$0.0022\ f^{1.98}$
Ethanol	C_2H_6O	78	776	1115	1142	$0.0048\ f^2$	$0.0045\ f^{2.00}$
Castor oil	$C_{18}H_{34}O_3$	313	952 (25°C)	1475	1508 – 1561	$f^{1.7}$	$0.553\ f^{1.59}$
Perfluorohexane	C_6F_{14}	59	1648	479	480 – 484	-	$\}0.352\ f^{1.56}$
Perfluoroheptane	C_7F_{16}	80	1695	514	516 – 521	-	
FC-77	$C_8F_{18} + C_8F_{18}O$	97	1750	550	557 – 566	-	

Physical properties, phase velocity and attenuation of the six liquids used in this study, along with a comparison to other published results. The measured attenuation of the three PFC liquids was similar, therefore a single fit was performed to the combined attenuation spectra.

attenuation was $0.0045f^{2.00}$ dB/cm/MHz^n, close to the published values of 1115 m/s [12] and $0.0048f^{2.00}$ dB/cm/MHz^2 [11]. No change in phase velocity from 100-1000 MHz was detected for water and ethanol. For castor oil, the measured sound speed was 1508 m/s at 200 MHz, and 1561 m/s at 700 MHz. Other studies have measured a sound speed of 1475 m/s [13], 1460 m/s [3] and 1472 m/s [5] around 36ºC using less than 30 MHz. The measured attenuation of castor oil was $0.553f^{1.59}$ dB/cm/MHz^n. Other studies measured the attenuation of castor oil as $0.5f^{1.74}$ dB/cm/MHz^n [13], $0.26f^{1.72}$ dB/cm/MHz^n [3] and $0.354f^{1.74}$ dB/cm/MHz^n [5] around 36ºC and frequencies from 3-30 MHz. In these studies a higher power exponent n was measured compared to this work, however n has been shown to decrease with increasing frequency, from 1.6 at 20 MHz to 1.4 at 100 MHz, at 23ºC [14]. Good agreement in both phase velocity and attenuation to published studies indicates the photoacoustic method is a reliable method to measure the phase velocity and attenuation of liquids. All results including a comparison to other studies are summarized in table I.

B. Perfluorocarbon Measurements

The measured phase velocity and attenuation of perfluorohexane, perfluoroheptane and FC-77 are shown in figure 2c-d. The phase velocity was 480, 516 and 557 m/s at 200 MHz for perfluorohexane, perfluoroheptane and FC-77, respectively. These measurements are similar to those made by Marsh et al at 36ºC [15]. Marsh et al did not measure FC-77, however FC-77 is composed of two compounds C_8F_{18} and $C_8F_{18}O$, which Marsh found to have similar sound speeds and is similar to our measurement. All three liquids exhibited slight dispersion with phase velocity increasing by approximately 1.5% from 200 to 700 MHz. The attenuation was similar for the three liquids, therefore a single fit of the three combined spectra was used. The attenuation was $0.352\ f^{1.56}$ dB/cm/MHz^n, and similar to castor oil, despite a different viscosity, sound speed and molecular structure.

Our research uses UHF ultrasonic and photoacoustic methods to characterize micron-sized PFC droplets, which can be used as contrast agents or for cancer therapy [16]. In our studies, the photoacoustic response from droplets showed good agreement to theoretical predictions, however some discrepancies in spectral features were attributed to changes in sound speed with frequency [17]. This technique was developed to measure the phase velocity of PFC liquids at UHF to improve the agreement between theory and experimental results.

V. CONCLUSIONS

This paper demonstrates a method to measure the phase velocity and attenuation of liquids using a photoacoustic method from 100-1000 MHz. Water, ethanol and castor oil were used to verify the methodology. PFC liquids exhibited slight dispersion, with an increase of 1.5% in the sound velocity from 200 to 700 MHz. Additionally, the PFC liquids had very similar attenuation spectra, which were similar to castor oil.

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