Seeking shear waves in liquids with picosecond ultrasonics

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Abstract. Picosecond shear acoustic pulses can be generated in solids using ultrashort optical pulses. Here we use this technique to seek high frequency shear waves in water, ethylene glycol and glycerol while simultaneously measuring high frequency longitudinal wave velocity and attenuation. We use a silica thin film on (114) GaAs to generate shear and longitudinal acoustic pulses at frequencies up to ~50 GHz by ultrashort pulsed optical excitation. The acoustic pulses are transmitted into adjacent liquids, and are detected through variations in the optical reflectivity. Although we could not detect shear waves in these liquids, we did detect gigahertz longitudinal elastic stiffening.

1. Introduction

At low frequencies liquids support only longitudinal sound waves. At higher frequencies the dynamical properties of liquids move from the hydrodynamic regime (liquid-like or viscous behaviour) to the elastic regime (solid-like behaviour). Shear waves may be observed in liquids when the acoustic frequency exceeds the relaxation rate for viscous effects, estimated in the Maxwell rheological model for structural relaxation as \( f_{\text{shear}} \geq G_\infty / 2\pi \eta \), where \( G_\infty \) is the shear modulus at infinite frequency and \( \eta \) is the viscosity. For water at 20 °C, \( f_{\text{shear}} \sim 160 \) GHz, where \( G_\infty \sim 10^9 \) Pa and \( \eta \sim 10^{-3} \) Pa s, although shear elastic effects at much lower frequencies are detectable. [1] Liquids of higher viscosity have lower values of \( f_{\text{shear}} \) (e.g., at ~0.3 GHz in glycerol at 20 °C). [2] Shear waves have been directly detected in liquids at gigahertz frequencies by Brillouin scattering (see, e.g., [3]).

It was recently shown that picosecond laser excitation of anisotropic materials can launch gigahertz shear acoustic pulses in addition to longitudinal acoustic pulses in solids. [4] In the present study we extend this method to probe picosecond acoustic waves generated in a (114) GaAs substrate coated with a thin silica film. Isotropic thermal expansion of the GaAs after the pulsed laser excitation produces quasishear and quasilongitudinal acoustic pulses that propagate away from the silica-GaAs interface as pure shear and longitudinal pulses in the silica. The acoustic pulses are then transmitted to a surrounding liquid. A principal aim of the experiment is to determine if the shear pulses are also coupled to and propagate in the liquid at the gigahertz acoustic frequencies in question.

We detect acoustic pulses in two ways: (i) through oscillations arising from interference between surface-reflected light and light reflected from moving acoustic wavefronts, and (ii) through abrupt changes in reflectivity caused by a combination of the deflection of sample interfaces and by the photoelastic effect in GaAs (that allows pulse-echo type detection). The first method is possible if the propagating strain perturbs the permittivity tensor, and is particularly noticeable in transparent media. As the sound waves propagate, the interference moves through maxima and minima with a frequency
determined by the wavelength of the probe light in the material ($\lambda/n$), the angle of refraction inside the material ($\theta$), and the sound velocity ($v_i$):

$$f_i = 2n v_i \cos \theta / \lambda.$$  

(1)

The oscillation frequency $f_i$ is precisely equal to the frequency of the strain wave component responsible for the optical scattering in transparent materials.

For isotropic media, such as the silica layer, Matsuda and Wright [5] found that optical reflection from propagating shear-strain is observable when (i) the incoming probe light has a polarization axis at 45° to the plane of incidence and the outgoing probe light is selected for $s$- or $p$-polarization, and (ii) the shear is perpendicular to the plane of optical incidence and the probe is at oblique incidence. This method is sensitive to the induced off-diagonal component of the permittivity tensor. In GaAs shear strain produces both diagonal and off-diagonal perturbations to this tensor, and so shear strain can be observed with either normal or oblique probe incidence. Here we use oblique (45°) probe incidence.

**Figure 1.** a) Transient relative reflectivity changes ($\lambda_{probe} = 815$ nm; incoming probe polarization at 45°, outgoing s-polarized.) before (lower curve) and after (upper curve, scale x 10) removal of an exponential cooling term. b) Fourier transform of the data in a), showing oscillations at 44.6 ± 0.3 and 27.3 ± 0.3 GHz. The peak at 1.3 GHz is an artefact of the delay line scanning.

2. Experimental Measurements

The experimental configuration is a standard optical pump-probe set-up. [4] The sample is a (114) GaAs wafer with a sputter-deposited 0.2 μm silica film. The sample is mounted in a quartz cell that holds liquid in contact with the surface. A frequency-doubled blue pump pulse ($\lambda_{pump} = 407.5$ nm) from an 82 MHz Ti:sapphire laser is normally incident on the sample and focused at the silica/GaAs interface, with an estimated spot radius, $r \sim 25 \mu m$, and a maximum fluence $\sim 15 J cm^{-2}$. The probe light, at 45° incidence, is either split from the frequency-doubled beam or from the primary beam, and has a similar fluence but tighter focus ($r \sim 12 \mu m$). All measurements were taken at ~20 °C.

2.1 Interference Oscillations due to Sound Pulses in (114) GaAs

Transient relative reflectivity ($\Delta R/R$) measurements with red (815 nm) probe light clearly show oscillations owing to probe reflection from sound pulses in the GaAs (see Fig. 1). The expected oscillation frequencies (from Eq. (1) with probe light incident at 45°, $n_{GaAs} = 3.66$, and $\theta = 11.1°$) are 44.7 and 26.4 GHz for quasilongitudinal ($v_{QL} = 5044$ ms$^{-1}$) and quasishear ($v_{SL} = 2982$ ms$^{-1}$) waves, respectively, along the [114] direction. A pure shear mode with an oscillation frequency of 29.8 GHz ($v_S = 3365$ ms$^{-1}$) does not couple with the laser light (cf., Ref. [4]). The observed oscillation frequencies are in very good agreement with these predictions (see Fig. 1b).

2.2 Pulse-echo Measurements

Transient relative echo measurements with blue (407.5 nm) probe light show effects of both the motion of the GaAs-silica interface and the photoelastic effect in GaAs (see Fig. 2a). A strong echo at 123 ps (labelled T in Fig. 2), corresponding to the time taken by the shear acoustic pulse to travel from the GaAs-silica interface to the free silica surface and back again, indicates that a significant fraction
of the shear pulse generated in the GaAs is transmitted to the silica. The ratio of the transverse to longitudinal echo time (72 ps/123 ps = .59) agrees well with the ratio of the known acoustic velocities in silica (3250/5460 = 0.6). A clear second longitudinal echo (labelled 2L) is observed near 144 ps, but subsequent echoes are relatively weak. Interference oscillations from sound pulses in the silica are expected at 18 and 32 GHz. However, because the periods of these oscillations are on the same order as the total propagation time in the film, they are not clearly resolved.

Figure 2. Transient relative reflectivity changes after exponential background subtraction ($\lambda_{\text{probe}}$= 407.5 nm; incoming probe 45° polarization, outgoing probe s-polarized).

a) Sample surface in air.

b) Sample surface in water. L: longitudinal, T: transverse echoes.

2.3 Interference Oscillations due to Sound Pulses in Liquids

Fig. 2b shows the measured reflectivity when water is in contact with the sample. The longitudinal sound pulse in the silica, incident upon the water-silica interface at 36 ps, launches a longitudinal pulse in the water that strongly interacts with the probe light. The associated interference oscillations have a frequency of $8.7 \pm 0.3$ GHz, as determined from the Fourier transform. This corresponds to a longitudinal acoustic velocity in water of $v_L = 1570 \pm 50$ ms$^{-1}$, ~5% larger than $v_L$ (1480 ms$^{-1}$) measured at 20 °C with conventional ultrasound at low frequencies or that determined from light scattering experiments up to 5 GHz. [6,7] It is also larger than the value of 1500 ms$^{-1}$ measured by Shelton and co-authors using picosecond ultrasonics with ~4 GHz longitudinal waves launched by photoexcitation of an Al film. [8] Pressure- or temperature-dependent changes in $v_L$ in these experiments can be ruled out as a possible explanation. Water-surface interactions may contribute to stiffening effects in the near surface region, but are not likely to affect $v_L$ at the distances from the surface (up to ~1 μm) involved here. Further experiments would help clarify the origin of the apparent stiffening we see.

Similar signals are observed in ethylene glycol and glycerol, which, as in the case of water, show only longitudinal interference oscillations even when probed with a configuration sensitive to shear waves in isotropic media (as for the data of Fig. 2). The oscillation frequency in ethylene glycol ($f_L$ =12.0 ± 1.3 GHz) corresponds to $v_L = 2000 \pm 200$ ms$^{-1}$, significantly greater than the low frequency value (1660 ms$^{-1}$) and that found from Brillouin scattering at ~5 GHz. [6, 9] However, our somewhat noisy data for this liquid preclude an accurate comparison. For glycerol (for which $f_L$ =18.7 ± 1.3 GHz) we find $v_L = 3000 \pm 200$ ms$^{-1}$, 50% above the low frequency value (1900 ms$^{-1}$) but in good agreement with the value extracted from Brillouin scattering data at ~20 GHz. [10] This stiffening is the signature of structural relaxation. [10]

Gigahertz shear acoustic propagation is strongly damped in liquids for $f < f_{\text{shear}} = G_{\nu} \times 2\pi \eta$, hence our failure to observe gigahertz shear waves in water ($f_{\text{shear}} \sim 160$ GHz). [1,7] There is more hope, however, for glycerol ($f_{\text{shear}} \sim 0.3$ GHz), which has the highest viscosity of our three liquids. Glorieux et al. [11] report a shear wave velocity in glycerol of 800 ms$^{-1}$ and strong attenuation from measurements of ~0.1 GHz interface modes. Scarponi et al. [12] have observed a shear velocity in glycerol of 1400 ms$^{-1}$ from well-defined shear modes at gigahertz frequencies from Brillouin scattering at 20 °C. Our failure to observe gigahertz shear waves in this liquid is probably caused by the small value of the photoelastic constant responsible for coupling shear oscillations to light. [12] Ethylene glycol is an
intermediate case, but our measured strong longitudinal wave attenuation at gigahertz frequencies (see Fig. 3) suggests that direct shear wave detection should be difficult. [9]

The attenuation for longitudinal waves can be estimated by fitting to a decaying oscillation,

$$\frac{\partial R}{\partial R} = Ae^{-\gamma t} \cos(2\pi f_L t + \phi_1) + B \cos(2\pi f_B t + \phi_2).$$  \hspace{1cm} (2)$$

where $\gamma$ is the attenuation rate of the sound wave in the liquid, as shown by the fits in Fig. 3 and the associated Table (that shows $\gamma^{-1}$ together with $n$ and the experimental values of $f_B$). The second term in Eq. (2) is an instrumental artifact associated with in the optical delay line scanning that produces a lower frequency oscillation. Owing to the low signal-to-noise ratio and the few oscillation cycles in the ethylene glycol data, the frequency $f_L$ and decay time ($\gamma^{-1}$) are only approximate for this liquid. Our values for $\gamma f^2$ are similar in order to those found in other gigahertz experiments for these liquids, where $f$ is the ultrasonic frequency. [7, 9, 13]

|          | $n$   | $f_L$ (GHz) | $\gamma^{-1}$ (ps) |
|----------|-------|-------------|---------------------|
| Water    | 1.33  | 8.7         | 550                 |
| Ethylene Glycol | 1.43 | ~12        | ~120                |
| Glycerol | 1.47  | 18.7        | 185                 |

Figure 3 Transient relative reflectivity changes with fits to Eq. 2 ($\lambda_{probe}= 407.5$ nm; incoming and outgoing probe s-polarized). Top: water; Middle: ethylene glycol; Bottom: glycerol.

3. Conclusions

In conclusion, we have measured the transmission of high frequency longitudinal acoustic pulses at a solid-liquid interface using water, ethylene glycol, and glycerol. The data yield accurate measurements of the longitudinal sound velocity in a small liquid volume at ~10-20 GHz. We find evidence for longitudinal acoustic stiffening in these liquids, but no evidence of shear wave propagation. Any detectable shear waves have, from Eq. (1), a lower frequency than the corresponding longitudinal waves. To overcome this frequency limitation of the photoelastic detection in the liquid, one could search for shear or longitudinal acoustic waves transmitted through thin liquid films. Measurements at lower temperatures or higher pressures would also be interesting.

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