High frequency longitudinal and shear acoustic waves in glass-forming liquids

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Abstract. Three different picosecond ultrasonic techniques for longitudinal and transverse acoustic pulse generation have been combined with Impulsive Stimulated Thermal Scattering (ISTS) to probe structural relaxation dynamics in glycerol and DC704 (tetramethyl tetraphenyl trisiloxane) at megahertz and gigahertz frequencies (~ 50 MHz - 100 GHz) from below their respective glass transition temperatures up to 370 K.

1. Introduction
Collective dynamics of glass-forming liquids remain a major scientific challenge in condensed matter [1]. Ultimately, these dynamics are described in terms of density and shear relaxation, so longitudinal and transverse acoustic modes carry the key information. However, significant dynamical gaps remain unexplored due to the experimental inaccessibility of the fast time scales (high acoustic frequencies) on which much of the correlation among motions of particles is lost. To close this gap, we have used a unique pulse shaping and spectroscopic approach where we adapt different laser ultrasonics techniques [2, 3, 4] to directly probe the MHz and GHz frequency longitudinal and transverse responses of glass forming liquids.

2. Experimental Approach and Results
For experiments in the Megahertz frequency range we used the technique of Impulsive Stimulates Thermal Scattering [5] where two crossed laser pulses intersect with each other in the sample and produce a spatially varying heating pattern. As depicted in Figure 1 (case 1), a single pulse from a short-pulse laser system is selected, split into two parts, and the two pulses intersected within the sample at an experimentalist-defined angle. The result is an interference pattern - or grating - of laser intensity inside the sample. This optical grating lasts for only the duration of the laser pulse, and given the short nature of the exciting pulses compared to any acoustic oscillation period, the material is driven impulsively. The excitation so generated shares the grating character of the optical excitation pattern, in particular its spacing which defines the acoustic wave vector and the time evolution of the scattered probe beam monitors the interaction of the acoustic wave with the liquid.
Figure 1. (Left) Schematic illustration of optical pulse shaper. A pulse is introduced in the system and makes seven round trips, each time slightly displaced, so that seven evenly spaced pulses emerge. The temporal interval between pulses can be changed by movement of a single delay line, permitting generation of pulse sequences with GHz-THz repetition rates. (Center) Schematic description of Impulsive Stimulated Scattering for MHz frequency acoustics (case 1). Two ultrashort pump pulses, shown here in grey, are incident on the sample with relative angle $\theta$ to generate a grating pattern of wavelength $\Lambda = \lambda/2\sin(\theta/2)$, where $\lambda$ is the wavelength of the light. A probe beam, designated in black, is incident upon the grating at the Bragg angle, and exchanges energy and momentum with material excitations of the grating wavevector. The coherently scattered probe light, shown here by the dashed line, is recorded in the time-domain by an amplified photodetector. (Right) Sample design with front-back excitation-probe geometry for generation and detection of acoustic pulses in the GHz frequency range. The optical output of the pulse shaper gets absorbed in a thin metal transducer film and thermal expansion launches a compressional strain pulse sequence into the depth of the sample. Various geometries have been employed to detect the acoustic pulse train: In case 2, Brillouin scattering of the probe light by the propagating acoustic pulse is used to directly monitor the interaction with the liquid. For cases 3 and 4, variable thicknesses of thin liquid layers (several nm up to 500 nm) have been combined with either interferometric detection in a receiver film or time-domain Brillouin scattering in a detection substrate in order to reach higher acoustic frequencies.

For higher frequencies we employed a front-back pump-probe type geometry where longitudinal and transverse acoustic waves are optically generated in a thin metal transducer film upon ultrafast laser irradiation [2]. To enhance weak signal levels, a novel pulse shaping method is used to generate multiple-cycle acoustic waves at GHz frequencies [7]. These acoustic waves are transmitted into an adjacent liquid layer and either directly detected in the liquid via Brillouin scattering (case 2, Figure 1), in an opaque metallic film at the other side of the liquid via interferometry (case 3) or in a transparent substrate in which they are detected through time-domain coherent depolarized Brillouin scattering (case 4). For transverse wave generation, a film with canted out-of-plane crystallographic orientation is used [3, 8]. The density and shear relaxation dynamics of the liquid are revealed through the measured acoustic frequency-dependent damping and dispersion.

Fourier spectral analysis of acoustic waves transmitted through different liquid thicknesses allows the extraction of a relative phase and attenuation for each set of recorded data. Liquid layers of different thicknesses are accessed by means of confining the liquid between two substrates (with one of them slightly curved) and moving the sample in the plane of the liquid layer by a motorized stage. From the comparison of any two individual sets of data from different sample regions with different liquid layer thickness, it is possible to calculate the phase difference.
and attenuation due to the thickness difference. The phase difference and attenuation directly yield the acoustic speed and attenuation rate at the selected acoustic frequency and sample temperature without the necessity of knowing any further material parameters for the specific sample [6].

The liquid response can be expressed in terms of a complex modulus, \( \hat{M}(\omega) = \rho \nu^2 \) (with given sample density \( \rho \)) being the longitudinal modulus \( \hat{M}(\omega) \) for longitudinal and the shear modulus \( \hat{G}(\omega) \) for transverse waves. The complex velocity is defined by \( \nu(\omega) = \omega / \hat{q}(\omega) \) through the complex wave vector \( \hat{q}(\omega) = q' + iq'' = \omega / \nu(\omega) + i\alpha(\omega) \), where \( \nu(\omega) \) is the frequency dependent speed of sound and \( \alpha(\omega) \) the frequency dependent acoustic attenuation. The obtained results are shown in Figure 2.

Figure 2. The rates measured longitudinal and shear sound velocities (A) and acoustic attenuation (B) for glycerol at room temperature as a function of frequency. The complex acoustic moduli spectra, the longitudinal modulus \( \hat{M}(\omega) = M' + iM'' \) (C) and the shear modulus \( \hat{G}(\omega) = G' + iG'' \) (D), can be calculated as described in the text.

In Figure 3, the measured acoustic frequencies and damping rates, respectively, as a function of temperature are shown for a variety of wavevectors ranging from 38.1 \( \mu m \) down to 0.121 \( \mu m \). This corresponds to acoustic frequencies from \( \sim 50 \) MHz up to \( \sim 20 \) GHz. The data show all the features consistent with the material undergoing a transition from liquid to glass: for high temperatures, the acoustic damping rate is low, then increases considerably when the alpha peak is in the probed region, and finally recedes again in the glassy regime. The acoustic velocity evolves linearly with temperature in the high and low temperature limits, allowing deduction of the zero and infinite frequency acoustic velocities \( c_0 \) and \( c_\infty \), respectively, and displays significant dispersion in the regime of the alpha relaxation.

3. Conclusion
Glass-forming liquids show two prominent features in their relaxation dynamics, a fast (picosecond time scale) “beta” regime revealed through the present GHz-frequency acoustic measurements and a slower, highly non-exponential, temperature-dependent “alpha” regime.
Figure 3. (A) Acoustic velocity in DC704 as a function of temperature for four wavevectors. Also plotted are linear extrapolations for the values of $c_0$ and $c_\infty$. (B) Scaled acoustic damping rate in DC704, where the scaling has been done by multiplying by the acoustic wavelength $\lambda$. The damping rates for higher wavevector are much larger due to the $\sim q^2$ background damping.

Phenomenological models and, in recent years, a first-principle theoretical framework (mode-coupling theory) have been advanced to describe the temperature-dependent dynamics as reflected in the frequency-dependent moduli [9]. Our experiments yield direct access to structural relaxation dynamics throughout both regimes over a wide temperature range, and permit direct testing of theoretical predictions of a quantitative relationship between the fast and slow dynamics (power-law exponent relations reminiscent of critical phenomena) that has remained untested to date due to the absence of the GHz-frequency acoustic data that we can now record. Work toward a comprehensive assessment of the theory is currently under way.

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