Observation of the onset of strong scattering on high frequency acoustic phonons in densified silica glass

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The linewidth of longitudinal acoustic waves in densified silica glass is obtained by inelastic x-ray scattering. It increases with a high power α of the frequency up to a crossover where the waves experience strong scattering. We find that α is at least 4, and probably larger. Resonance and hybridization of acoustic waves with the boson-peak modes seems to be a more likely explanation for these findings than Rayleigh scattering from disorder.

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A controversy regarding the fate of very high frequency acoustic-like excitations in glasses arose in recent years [1, 2]. Acoustic waves propagate in glasses up to rather high frequencies, for example up to at least $\Omega/2\pi \simeq 0.4$ THz in vitreous silica, $\text{v-SiO}_2$ [3, 4]. However, silica shows a pronounced “plateau” in the temperature ($T$) dependence of its thermal conductivity $\kappa(T)$ [5]. This feature was explained by postulating the existence of a rapid crossover of acoustic waves into a regime where they experience strong scattering [6]. In $\text{v-SiO}_2$, this crossover is expected at a frequency $\Omega_{co}/2\pi \simeq 1$ THz [7]. For the observed horizontal plateau to occur, besides strong scattering of thermal phonons, phonons of lower $\Omega$ must also experience a sufficiently strong $T$-independent scattering [8]. Several models predict that the inhomogeneous width of acoustic waves can increase with a high power of $\Omega$, typically in $\Omega^4$ [3, 10], leading to this rapid crossover. However, the origin of the high power remained debated, whether Rayleigh scattering from structural defects [4], or resonance with local modes [10, 11, 12]. Rayleigh scattering seems generally too weak in materials as homogeneous as dense glasses to be able to account for the relatively low $\Omega_{co}$ suggested by the position of the plateau [6, 8]. The local modes are seen in the “boson peak” (BP) and produce an excess over the Debye specific heat [13]. Successful models based on resonance or on soft potentials were developed to describe the observed properties, e.g. in [10, 14, 15].

It might seem, judging from some recent literature [2], that the above picture should be revised after it became possible to observe in glasses the spectrum of longitudinal acoustic (LA) waves at THz frequencies with x-ray Brillouin scattering (BS) [16]. This new experimental tool is important here, as it potentially allows to check some of the previous conjectures. It led to many publications claiming to prove that sound propagates at frequencies much above the early expectations for $\Omega_{co}$, e.g. [17, 18]. In this respect, it must be emphasized that inelastic x-ray scattering (IXS) still is a difficult spectroscopy with severe limitations on resolution and intensity. Firstly, it is practically not possible with current instruments to investigate scattering vectors $Q$ below $\sim 1$ nm$^{-1}$, a value which happens to coincide with the expected wave vector $q$ at crossover, $q_{co}$, in $\text{v-SiO}_2$ [14] and in many other glasses. Secondly, the narrowest instrumental profile allowing for sufficient intensity [19] still has an energy width around 1.5 meV (or $\simeq 0.4$ THz) and extended Lorentzian-like wings. Owing to the relatively strong elastic scattering of glasses, this tends to mask the weaker Brillouin signal. For these reasons it is still not possible to investigate with IXS the LA waves of $\text{v-SiO}_2$ at frequencies where their linewidth might grow in $\Omega^4$ [20, 21]. Finally, the signal-to-noise ratio being also small, the subtle changes in BS lineshapes that indicate strong scattering might easily go unnoticed [22]. To alleviate several of these difficulties, we investigated permanently densified silica glass, $d$-$\text{SiO}_2$, in which $\Omega_{co}/2\pi \simeq 2$ THz and $q_{co} \simeq 2$ nm$^{-1}$ [23, 24]. A clear demonstration of a rapid increase of the LA-width as $\Omega$ approaches $\Omega_{co}$ from below is still missing. This is a crucial check for the onset of strong scattering. It is all the more important that many recent Letters advocated acoustic linewidths that vary as $Q^2$ up to very high $Q$-values, denying the onset of strong scattering and the existence of the corresponding crossover, e.g. [17, 18, 22, 26, 27, 28, 29]. In this Letter, we use the window between the smallest accessible $Q$ and the $q_{co}$ of $d$-$\text{SiO}_2$ to study the approach of the crossover. We find a width in $\Omega^4$ with $\alpha$ at least equal to 4 and probably larger, corroborating the early intuition of a rapid crossover to strong scattering.

The experiments were performed on the high-resolution IXS spectrometer ID16 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The x-ray energy is 21.7 keV. The main components of the spectrometer are a $T$-scanned monochromator, the sample, a battery of five $T$-stabilized spherical analyzers, and the corresponding detectors. The instrumental lineshape was determined for each analyzer behind its standard slit of $20 \times 60$ mm (width$\times$height), using the signal from the first sharp diffraction peak of polymethyl...
methacrylate at 20 K. Very clean Voigt-like shapes were obtained with half-widths at half-maximum of \( \simeq 0.75 \) meV. The analyzers permit data collection at five \( Q \) in increments of \( \simeq 3 \) nm\(^{-1}\). As we are now interested in small \( Q \), the first analyzer was placed to the left of the forward direction, and the second to the right. This allows simultaneous collection of two interesting data points with \( Q \leq 2 \) nm\(^{-1}\). The data presented here were thus acquired with only three different positions of the first analyzer, \( |Q| = 2, 1.8, \) and \( 1.6 \) nm\(^{-1}\). Each spectrum was accumulated for nearly two full days. The sample of \( d\)-SiO\(_2\), of density 2.62 g/cm\(^3\), is the same as in previous measurements\[^{22,24}\]. It is heated at 565 K to increase the inelastic signal. At this \( T \), the densified structure does not relax. This was subsequently checked with optical BS, the sound velocity providing a sensitive test for the density\[^{22}\].

Figure 1 illustrates typical spectra and their fits. The indicated values of \( Q \) correspond to the center of the collection slit which gives a spread \( \Delta Q \simeq \pm 0.18 \) nm\(^{-1}\). The spectra consist in a strong elastic peak plus a weaker Brillouin doublet. In Fig. 1a, the full raw spectrum is shown for the smallest usable \( Q \), namely \( Q = 1.17 \) nm\(^{-1}\)\[^{30}\]. The dashed line follows the elastic peak, illustrating the relative weakness of the doublet. To extract information on the position \( \Omega \) and half-width \( \Gamma \), the spectra are first adjusted to a damped harmonic oscillator (DHO) profile plus an elastic central peak (CP), convoluted with the instrumental function. Account is taken of the broadening due to the collection angle by summing over contributions from surface elements of the slit, each at its own \( Q \), using \( d\Omega/dQ = v_g \). Here \( v_g \) is the group velocity which is determined iteratively. There are four free parameters in the fits: the integrated intensities of the elastic (\( I_{\mathrm{CP}} \)) and inelastic (\( I_{\mathrm{DHO}} \)) components, \( \Omega \) and \( \Gamma \). The small background shown by the baselines is fixed to the detector noise, measured independently. Figs. 1b,c illustrate, for the two extreme values of \( Q \) measured below crossover, the inelastic part that remains after subtraction of the adjusted elastic contribution \( I_{\mathrm{CP}} \). The solid lines are the DHO fits. In Fig. 1b the width is mostly instrumental, while in 1c it is due to a large part to a real broadening of the Brillouin signal.

The values obtained for \( \Gamma \) are shown in Fig. 2 against those for \( \Omega \) which agree with\[^{22}\]. \( \Gamma \) increases very rapidly with \( \Omega \). There should be a homogeneous broadening contribution to this width, \( \Gamma_{\mathrm{hom}} \). It is estimated from \( \Gamma_{\mathrm{hom}} \propto \Omega^2 \) by extrapolation of an optical BS determination, \( \Gamma_{\mathrm{hom}}/2\pi = 26 \pm 5 \) MHz for \( \Omega/2\pi = 41.5 \) GHz at 600 K\[^{31}\]. Interestingly, that BS experiment the linewidths of \( d\)-SiO\(_2\) are very near those of crystal quartz over a broad range of \( T \), whereas the linewidths of \( \nu\)-SiO\(_2\) are typically four times larger. Thus, it seems reasonable to assume \( \Gamma_{\mathrm{hom}} \propto \Omega^2 \), as e.g. the Akhiezer mechanism might extend up to the THz region in \( d\)-SiO\(_2\) at these elevated \( T \)-value. This gives the \( \Gamma_{\mathrm{hom}} \) drawn in Fig. 2. The total rate is then approximated by Matthiesen’s rule of adding rates due to independent processes, \( \Gamma = \Gamma_{\mathrm{hom}} + \Gamma_{\mathrm{inh}} \)[^21]. The inhomogeneous scattering width is adjusted to \( \Gamma_{\mathrm{inh}} \propto \Omega^\alpha \). A fit of the five measured points with this expression gives the solid line in Fig. 2 with \( \alpha = 4.21 \pm 0.15 \), and \( \chi^2 = 0.76 \). For comparison, if we force \( \alpha = 2 \), the best fit shown by the dotted line gives \( \chi^2 = 5.4 \).

The inelastic intensities, \( I_{\mathrm{DHO}} \), derived from these fits are shown in the inset of Fig. 2. With the very clean in-
We find that \( \bar{\hbar} I \) is nearly equal to twice the observed one. This is precisely the saturation expected near crossover \[23\]. The value of \( \alpha \) obtained in this manner does not change by allowing for the uncertainty in \( \Gamma_{\text{hom}} \), only its uncertainty increases slightly. If \( \alpha \) is really so large, the onset of strong scattering of sound cannot be due to Rayleigh scattering from structural inhomogeneities which give \( \alpha = 4 \). 

Resonance of sound with point-like local modes, assuming a bilinear coupling, leads to \( \Gamma_{\text{inh}}(\Omega) \propto \rho(\Omega) \) where \( \rho(\Omega) \) is the mode density of states \( \text{(DOS)} \) \[10, 14\]. Fig. 3 shows the DOS of \( \alpha \)-SiO\(_2\) taken from \[33\] after subtraction of a Debye contribution of \( 1.44 \times 10^{-5} \times (\hbar \Omega)^2 \), with \( \hbar \Omega \) in meV. The BP, \( \rho(\Omega)/\Omega^2 \), with its maximum near \( \Omega_{\text{co}} \), \[24\], is also shown. The values of \( \Gamma_{\text{inh}} \) and \( \Gamma \) are drawn on the same plot for comparison. They increase together with \( \rho \) but do not seem exactly proportional to \( \rho \). There can be several reasons for this. One is that an exact determination of \( \rho(\Omega) \) with neutron scattering is always a difficult task, especially for \( \alpha \)-SiO\(_2\) as a large sample can contain a few less densified fragments. Another

![Graph](image-url)

**FIG. 2:** The linewidths \( \Gamma \) extracted from DHO fits. \( \Gamma_{\text{hom}} \) extrapolated from optical Brillouin scattering is shown by a full line terminated by dots. A full line \( (\alpha = 4.2) \) shows the fit to \( \Gamma_{\text{hom}} + \Gamma_{\text{inh}} \). The dashed line \( (\alpha = 5.7) \) is the same fit restricted to the four lowest data points. The dotted line illustrates the best fit with \( \alpha = 2 \), i.e. with \( \hbar Q^2 \). The inset shows the total inelastic intensities (dots) normalized to 5 hours accumulation on the best analyser (#2) compared to a line \( \propto v_{\text{LA}}^{-2} \).

**FIG. 3:** The DOS of the local modes (squares) extracted from neutron scattering data \[33\] compared to \( \Gamma_{\text{inh}} \) (dots) and \( \Gamma \) (triangles). For illustration the boson peak calculated from this DOS is shown by the full line in \( 10^{-5} \text{ meV}^{-3} \).
As final remark we stress that a logarithmic presentation of $\Gamma(Q)$ over a large range of $Q$ (Fig. 4) for the optical Brillouin scattering point [31] and the IXS data obtained here. The straight line gives a power $\gamma = 2.47$ which averages over different regimes and which is of no further significance.

The line is a fit with $\Gamma \propto q^4$. This is illustrated in Fig. 4 for the data presentation of $\Gamma(q)$ over a large range of $Q$. The rapidly growing $\Gamma$ is unfounded. In Fig. 4, the lowest $Q$ point is purely homogeneously broadened, the next four points are dominated by inhomogeneous broadening, the sixth point is near crossover, and the following three points are well above crossover. Hence, that presentation averages over three distinct regimes: one where $\Gamma = \Gamma_{\text{hom}}$, one which is dominated by $\Gamma_{\text{inh}}$, and finally one where $\Gamma$ should not be extracted from DHO fits. The rapidly growing $\Gamma_{\text{inh}}$ only dominates $\Gamma$ over a narrow range in $Q$ (or $q$). To be able to conclude about $\alpha$ as we do here, one needs: i) to know the position of $\Omega_{\text{co}}$ and, ii) to have a sufficient number of data points with significant values of $\Gamma$ just below $\Omega_{\text{co}}$. This was not the case in previous experiments, e.g. in [21] or in [35].

In this Letter, we reported the first spectroscopic observation of the onset of strong scattering of LA waves with $q < q_{\text{co}}$ in a network glass. In that region of $q$ the inhomogeneous linewidth grows with a very high power of $\Omega$, at least equal to 4, and probably higher. Also the intensity shows an anomalous increase with $q$. It seems that these results could be explained by the resonance and hybridization of the LA waves with the local BP modes. If so, these measurements might provide some information about the structure of glasses at extended length scales about which so little is known otherwise.

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