Non-dynamic origin of the acoustic attenuation at high frequency in glasses

G. Ruocco\textsuperscript{1}, F. Sette\textsuperscript{2}, R. Di Leonardo\textsuperscript{1}, D. Fioretto\textsuperscript{3}, M. Lorenzen\textsuperscript{2}, M. Krisch\textsuperscript{2}, C. Masciovecchio\textsuperscript{2}, G. Monaco\textsuperscript{1}, F. Pignon\textsuperscript{2}, T. Scopigno\textsuperscript{4}

\textsuperscript{1} Dipartimento di Fisica and INFM, Università di L’Aquila, I-67100, l’Aquila, Italy.
\textsuperscript{2} European Synchrotron Radiation Facility, BP 220, F-38043, Grenoble Cedex, France.
\textsuperscript{3} Dipartimento di Fisica and INFM, Università di Perugia, I-06100, Perugia, Italy.
\textsuperscript{4} Dipartimento di Fisica and INFN, Università di Trento, I-38050, Povo, Trento, Italy.

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The sound attenuation in the THz region is studied down to at T=16 K in glassy glycerol by inelastic x-ray scattering. At striking variance with the decrease found below \( \approx 100 \) K in the GHz data, the attenuation in the THz range does not show any \( T \) dependence. This result i) indicates the presence of two different attenuation mechanisms, active respectively in the high and low frequency limits; ii) demonstrates the non-dynamic origin of the attenuation of THz sound waves, and confirms a similar conclusion obtained in SiO\(_2\) glass by molecular dynamics; and iii) supports the low frequency attenuation mechanism proposed by Fabian and Allen (Phys.Rev.Lett. 82, 1478 (1999)).

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One of the most important and still unsettled subjects in the physics of topologically disordered systems regards the mechanisms for the propagation and attenuation of density fluctuations. The propagating nature of acoustic waves, as seen by Ultrasonic and Brillouin Light Scattering (BLS) measurements in the MHz and GHz region respectively, has been shown to persist up to the THz region by the existence of a linear relation between the peak energy, \( E \), and the momentum transfer, \( Q \), of the inelastic features observed in the dynamic structure factor, \( S(Q, E) \), of glasses \[\textsuperscript{1}\]. This result is the outcome of extensive studies on the shape of \( S(Q, E) \) performed using Molecular Dynamics (MD) simulations \[\textsuperscript{2,3}\] and the newly developed Inelastic X-rays Scattering (IXS) technique \[\textsuperscript{4,5}\]. This latter technique allows to study the \( S(Q, E) \) in the "high" \( Q \) range \( (Q \approx 1-10 \text{ nm}^{-1}) \), thus increasing by about two orders of magnitude the \( Q \) values typically investigated by BLS \( (Q \approx 0.01-0.04 \text{ nm}^{-1}) \).

In the IXS and MD \( Q \)-range, beside the persistence of a linear dispersion of the acoustic excitation energies, one also observes a progressive broadening of the inelastic features, which is responsible for their disappearance at a certain \( Q_m \) value. Typically \( Q_m \) is some tenths of \( Q_M \) – the position of the first sharp diffraction peak in the static structure factor, \( S(Q) \) \[\textsuperscript{6}\]. The study of the mechanisms leading to this damping, and, therefore, the investigation of the sound waves attenuation at these \( Q \) values – characteristic of structural correlations at the interparticle level – is obviously of great interest.

The acoustic excitations at frequencies in the THz range, as measured so far in glasses and glass forming liquids by IXS, have a linewidth parameter \( \Gamma_Q \) which seems to show a \( Q^2 \) dependence \[\textsuperscript{7}\]. Moreover – in all the IXS data reported so far – \( \Gamma_Q/Q^2 \) has a negligible temperature dependence in a wide temperature range ranging from values well below the glass transition temperature, \( T_g \), up to the liquid phase \[\textsuperscript{8}\]. At variance with this behavior, as well known, the linewidth of the excitations in the GHz region, measured by BLS, show a relevant temperature dependence, which becomes particularly strong in the limit of very small temperatures \[\textsuperscript{9}\]. The temperature dependence of the linewidth in the GHz range has motivated many theoretical studies, leading to different hypotheses on the frequency (or \( Q \)) evolution of the attenuation mechanisms \[\textsuperscript{10}\].

In this Letter we report an IXS study on the low temperature behavior of the excitations linewidth in glassy glycerol. Specifically, we concentrate on the study of THz excitations in the temperature region where the BLS data in the GHz range show a marked temperature variation. Within the error bar, the linewidth measured by IXS is \textit{temperature-independent} in the whole 0.1\( T_g \) to \( T_g \) region, whereas, in this same region, the BLS linewidth increases by more than a factor of ten. This two opposit behaviors indicate that there are at least two different attenuation mechanisms: i) One of dynamic origin dominant in the low \( Q \) (low frequency) region, and ii) A second one, dominant at high \( Q \), whose temperature independence suggests that its origin is due to the structural disorder of the glass. The glycerol results are confirmed by a similar sound attenuation behavior found in vitreous silica, as obtained by the analysis of existing BLS, IXS and MD data. The observation of two distinct attenuation mechanisms, each one dominant in a different \( Q \) region, implies the existence of a cross-over frequency, which lies in the 100 GHz range for both of the studied glasses. It also suggests that the frequency dependence of the dynamic contribution to the sound attenuation agrees with the one recently predicted by Fabian and Allen \[\textsuperscript{11}\].

The experiment has been carried out at the new very high energy resolution IXS beamline ID28, at the European Synchrotron Radiation Facility. The incident x-ray beam is obtained by a back-scattering monochromator operating at the Si(11 11 11) reflection \[\textsuperscript{12}\]. The scattered photons are collected by a spherical silicon crystal analyzer, also operating at the Si(11 11 11) reflection \[\textsuperscript{13}\].

\[\textsuperscript{1}\] Dipartimento di Fisica and INFM, Università di L’Aquila, I-67100, l’Aquila, Italy.
\[\textsuperscript{2}\] European Synchrotron Radiation Facility, BP 220, F-38043, Grenoble Cedex, France.
\[\textsuperscript{3}\] Dipartimento di Fisica and INFM, Università di Perugia, I-06100, Perugia, Italy.
\[\textsuperscript{4}\] Dipartimento di Fisica and INFN, Università di Trento, I-38050, Povo, Trento, Italy.
\[\textsuperscript{5}\] M. Krisch
\[\textsuperscript{6}\] Dipartimento di Fisica and INFM, Università di L’Aquila, I -67100, l’Aquila, Italy.
\[\textsuperscript{7}\] Dipartimento di Fisica and INFM, Università di Perugia, I- 06100, Perugia, Italy.
\[\textsuperscript{8}\] Dipartimento di Fisica and INFM, Università di Trento, I-38050, Povo, Trento, Italy.
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The monochromatic beam has an energy of $\approx 21,748$ eV and an intensity of $2 \times 10^8$ photons/s. The total energy resolution — obtained from the measurement of $S(Q_M, E)$ in a Plexiglas sample which is dominated by elastic scattering — is $1.5$ meV full-width-half-maximum (fwhm). The momentum transfer, $Q = 2k_0\sin(\theta_s/2)$, with $k_0$ the wavenumber of the incident photon and $\theta_s$ the scattering angle, is selected between 2 and 4 nm$^{-1}$ by rotating a 7 m long analyser arm in the horizontal scattering plane. The total $Q$ resolution has been set to 0.2 nm$^{-1}$. Energy scans are done by varying the relative temperature between the monochromator and analyzer crystals. Each scan took about 180 min, and each $(Q, T)$-point spectrum has been obtained from the average of 2 to 8 scans depending on the sample temperature. The data have been normalized to the intensity of the incident beam. The sample cell is made out of a pyrex-glass tube (4 (10) mm inner (outer) diameter and 20 mm length), capped with two diamond single crystals discs, 1 mm thick, to minimize undesired scattering signals. The cell has been loaded with high purity glycerol in an argon glove box. In the $Q-E$ region of interest, empty cell measurements gave the flat electronic detector background of 0.6 counts/min. The cell length was chosen to be comparable to the x-ray photoabsorption length, and multiple scattering was negligible.

The spectra have been collected at $T=16, 45, 75, 114, 145$ and 167 K, and, as examples, those at $T = 16$ and 167 K are reported in Fig. 1 for different $Q$-values. The full lines are the fits to the data, obtained using a model function made by the convolution of the experimentally determined resolution function with a delta function for the elastic peak and a Damped Harmonic Oscillator (DHO) model for the inelastic peaks [1]. This model for the $S(Q, E)$ results from the assumption that the memory function, $m_Q(t)$ [19], entering in the Langevin equation for the considered $Q$-component of the density fluctuation, has a time dependence as: $m_Q(t) = 2\Gamma_Q(T)\delta(t) + \Delta_Q^2(T)$ [20]. The presence of the structural $\alpha$-relaxation, observed in the liquid state and frozen in the glass, and of other relaxation processes with characteristic times slower than $\approx 1$ ps, is reflected in the parameter $\Delta_Q(T)$, whose value determines the change of the sound velocity, $c$, between the fully relaxed ($c_\infty$) and unrelaxed ($c_g$) limiting values: $\Delta_Q^2(T) = Q^2(c_\infty^2 - c_g^2)$. The parameter $\Gamma_Q(T)$ determines the width of the side peaks, i. e. the sound wave attenuation coefficient, $\alpha = 2\pi\Gamma_Q/hc$. However, fits made with the DHO model or with different fitting function gave values for the FWHM of the inelastic peaks consistent among each other within their statistical uncertainties, indicating, therefore, the insensitivity of the results to the specific model for the inelastic peaks. As it is evident already from the raw data, $\Gamma_Q(T)$ has a marked $Q$-dependence while its $T$-dependence, if any, is much smaller. This is better seen by the dotted lines in Fig. 1, which represent the unconvoluted inelastic part of $S(Q, E)$.

The values of $\Gamma_Q(T)$ resulting from the fit of the IXS data of Fig. 1 are reported as a function of $Q$ in Fig. 2. In the same figure are also shown the $\Gamma_Q(T)$ obtained from IXS measurements at 175 K [1], and those obtained from literature BLS spectra measured at $Q \approx 0.03$ nm$^{-1}$ and temperatures similar to the IXS’ ones [9,21]. This figure demonstrates that, within the error bars, $\Gamma_Q(T)$ is $T$-independent in the $Q$ region covered by IXS. On the contrary, $\Gamma_Q(T)$ shows a marked $T$-dependence at the $Q$ value of the BLS measurements. These $T$-dependencies are emphasized in Fig. 3, where $\Gamma_Q(T)/Q^2$ is plotted as a function of $T$ for $Q$ in the BLS region ($Q \approx 0.035$ nm$^{-1}$) [22] and for $Q$ in the IXS region. Here the crossed symbols refer to IXS measurements at fixed $Q (Q = 2$ nm$^{-1}$) and the full symbols to the average of $\Gamma_Q(T)/Q^2$ over the $Q = 2 - 4$ nm$^{-1}$ region. This figure confirms that, at the high $Q$ values, $\Gamma_Q(T)$ is substantially constant even at very low $T$, whereas, at the low $Q$ values, it increases with temperature up to $\approx 100$ K, where it seems to reach a plateau. The further increase above $T_g$ is due to the $\alpha$-relaxation; it is only seen in the low $Q$ data as it would affect the high $Q$ data at higher $T$.

The specific dynamic mechanisms (anharmonicity, relaxation processes, floppy modes, two level systems...) at the origin of the acoustic attenuation observed at the BLS’ $Q$ values, as well as their temperature dependence, have been widely investigated in the past [13]. In contrast to what it is found in the BLS’ $Q$ region, the behavior of $\Gamma_Q(T)$ in the high $Q$ region, as reported in Figs. 2 and 3, shows that here the sound attenuation is not determined by temperature activated dynamic processes. Consequently, in this $Q$ range, at variance with the crystalline state where the absence of dynamic processes would imply no sound attenuation, in the glass the observed non vanishing value of $\Gamma_Q$ must have a ”structural” origin, i. e. it must be due to the topological disorder of the glass structure.

The picture coming from the reported data suggests that one can express $\Gamma_Q(T) = \Gamma_Q^{(d)}(T) + \Gamma_Q^{(s)}$, where $\Gamma_Q^{(d)}(T)$ is a temperature dependent dynamic part and $\Gamma_Q^{(s)}$ is due to topological disorder. The $Q$-dependence of $\Gamma_Q^{(d)}(T)$ must be such to be the dominant term of $\Gamma_Q(T)$ at small $Q$, while it must be negligible at large $Q$. This behavior is consistent with a recent calculation of the dynamic (anharmonicity) contribution to the sound attenuation by Fabian and Allen [13], who predict a $\Gamma_Q(T) \propto Q^2$ up to a $Q_c$ value, above which $\Gamma_Q(T) = const.$ In the case of amorphous silicon, $Q_c$ has been calculated to be in the 0.1 nm$^{-1}$ range [14]. Although there is no such calculation for glycerol, the present results indicate that also in this glass the crossover takes place at $Q$ values between the BLS’ and IXS’ ones, i. e. in the $\nu_c \approx 100$ GHz frequency range. It is worth to note that a relaxation process with characteristic time $\tau = 1/2\pi\nu_c \approx 2$ ps,
and responsible for a linewidth of the order $\Gamma_Q/Q^2 \approx 0.2$ meV/nm$^{-2}$, should also give a dispersion of the sound velocity, $\delta c$, given by $\delta c = \pi T_Q/Q^2 \tau c^2 \approx 1\%$, a value too small to be detectable with the achievable accuracy at present. Therefore, in the present case, the change of sound velocity cannot be used to estimate the crossover value $Q_c$.

The $Q$-dependence of $\Gamma_Q^{(s)}$, as already observed before in many other glasses and glass forming systems [1], is well represented by a $Q^2$ law, $\Gamma_Q^{(s)} = D Q^2$, in the $Q$ region covered by IXS. This $Q^2$ law, shown as a full line in Fig. 2, however, cannot be extrapolated (thin full line) to low $Q$ values because it would predict width values in excess to the measured $\Gamma_Q(T)$. This observation excludes that $\Gamma_Q^{(s)} \propto Q^2$ in the whole 0.01-10 nm$^{-1}$ $Q$ range. Under the hypothesis that $\Gamma_Q^{(s)} = Q^2$, and assuming that at the lowest measured temperature $\Gamma_Q^{(s)} = \Gamma_Q$, one finds consistency within the error bars of both the IXS data and the BLS low temperature point, as shown by the dashed line in Fig. 2 obtained with $\gamma = 2.5$. This estimate of $\gamma$ is a low limiting value, because the BLS low $T$ width could still be partially affected by a dynamic contribution. It is not clear, however, whether the hypothesized power law indeed provides a good representation of $\Gamma_Q^{(s)}$; some hints on this issue can be gathered by the study of other glasses.

The previous picture for the sound attenuation in the glycerol glass is further substantiated by the existing IXS [22–24], BLS [10–13,25], MD [5] and Picosecond Optical Technique (POT) [26], data in another prototypical glass: vitreous silica ($v$-$SiO_2$). We report in Figs. 4 and 5 the $\Gamma_Q(T)$ values for $v$-$SiO_2$ in a format equivalent to that of Figs. 2 and 3. In Fig. 4, the $\Gamma_Q(T)$ values in the 1 to 5 nm$^{-1}$ region, as obtained by IXS, do not show any relevant $T$-dependence in the 300-1450 K range. As a consequence of contrast problems due to the limited energy resolution of the IXS spectrometer, at temperatures below 300 K, it has not been possible to discriminate the inelastic signal from the tails of the elastic one. The missing low temperature IXS data are supplied by an extended MD simulation performed in the harmonic approximation ($T = 0$ K), which provides a $S(Q, E)$ lineshape in excellent agreement with the IXS data, and confirms the absence of any relevant $T$-dependence of the sound attenuation in the whole $T$=0-1450 K and $Q$=1-5 nm$^{-1}$ ranges. On the contrary, as in glycerol and as emphasized in Fig. 5, the BLS data of $v$-$SiO_2$ data show a large $T$-dependence. As in other glasses, also the high $Q$ $v$-$SiO_2$ data of $\Gamma_Q$ have a $Q$-dependence well represented by a $Q^2$ law (full line in Fig. 4). In $v$-$SiO_2$ are also available room $T$ data in a $Q$ region intermediate to BLS and IXS ($Q$=0.03-0.4 nm$^{-1}$), as obtained by POT. These data, however, show a relevant inconsistency with BLS data measured in the same $Q$ and $T$ ranges.

The similar behavior between $v$-$SiO_2$ and glycerol allows to formulate also for $v$-$SiO_2$ the same hypotheses on the $Q$ and $T$-dependencies of $\Gamma_Q^{(D)}(T)$ and $\Gamma_Q^{(s)}$. It is worth to note, however, that the ability of the power law for $\Gamma_Q^{(s)}$ (which should have $\gamma = 2.6$) to pass through all the IXS data and the low $T$ BLS point is substantially worse than in glycerol. Therefore the $v$-$SiO_2$ results clearly indicates that the power law hypothesis is wrong and that $\Gamma_Q^{(s)}$ has a more complex behavior, namely it is $\propto Q^2$ in the high $Q$ regime ($Q > 1$ nm$^{-1}$) and it has a steeper behavior at low $Q$ values.

In conclusion, we have shown that in glycerol and silica glasses the dominant sound attenuation mechanism has a different origin in the $Q$ region spanned by the IXS or BLS techniques. The temperature independence of the attenuation at large $Q$, corresponding to frequencies in the THz region, implies that its origin is structural and it is due to the disorder. On the contrary, the well known strong $T$-dependence found in the low $Q$ region, at GHz frequencies and below, implies a dynamic origin of the sound attenuation [2]. These findings imply a cross-over region between the two regimes, which should lie in the 100 GHz frequency range. The overall $T$ and $Q$-dependencies of the attenuation considered here is consistent with a dynamic ($\Gamma_Q^{(D)}$) part that closely follows the one proposed by Fabian and Allen [10], and a structural part ($\Gamma_Q^{(s)}$) that has a $Q^2$ behavior at high $Q$ ($Q > 1$ nm$^{-1}$) and a steeper $Q$ dependence at lower $Q$. The hypothesis on a cross-over between the two different attenuation mechanisms considered here call for further studies, where the $Q$ and $T$-dependencies of the sound waves is thoroughly investigated using the BLS and IXS technique in a wider number of glass materials.
FIGURE CAPTIONS

FIG. 1 - Inelastic x-ray scattering spectrum of glycerol at T=16 and 167 K and at the indicated Q-values. The full lines are the best fit to the data as discussed in the text. The dotted lines represent the uncorrected inelastic contributions to the fit.

FIG. 2 - The linewidth parameters $\Gamma_Q$ for glycerol are reported as a function of $Q$ at the indicated temperatures in the IXS' (full symbols) and BLS' (open symbols) $Q$ regions. The inset shows an enlargement of the IXS' $Q$ region. The full line represents the $Q^2$ behavior, which is the best fit to $\Gamma_Q$ at high $Q$. Also shown in the figure are extrapolation of the $Q^2$ law in the low $Q$ range (thin full line) and the $Q^{2.5}$ dependence (dashed line) indicated by the low $T$ BLS data. The inset shows an enlargement of the high $Q$ region.

FIG. 3 - Temperature dependence of $\Gamma_Q/Q^2$ in glycerol at $Q \approx 0.03$ nm$^{-1}$ (open symbols), at $Q = 2$ nm$^{-1}$ (crossed symbols) and averaged over the $Q = 2 - 4$ nm$^{-1}$ region (full symbols). The vertical dashed line indicates the glass transition temperature, $T_g=187$ K.

FIG. 4 - Same as in Fig. 2 but for vitreous silica. Data from MD simulation (crossed symbols) and from POT (stars) are also reported. Here the low $T$ BLS data indicate (if any) a power law with exponent $\gamma = 2.6$. The inset shows an enlargement of the high $Q$ region.

FIG. 5 - Same as in Fig. 2 but for vitreous silica. The inset shows an enlargement of the low temperature region. The open circle refer to BLS data at $Q \approx 0.035$ (○) and $Q \approx 0.025$ (◇) nm$^{-1}$, the full squares to IXS data at $Q = 1.6$ nm$^{-1}$, and the crossed circle to MD simulation in the harmonic (T= 0 K) limit. The inset shows an enlargement of the low $T$ region.
Glycerol

\[ \gamma = 2.5 \]

\( T = 16 \text{ K} \) (This work)
\( T = 167 \text{ K} \) (This work)
\( T = 175 \text{ K} \) [1]

\( T = 20 \text{ K} \) [9]
\( T = 170 \text{ K} \) [21]
This work

Ref. [6]

Ref. [1]

Ref. [7]

Ref. [8]

Ref. [9]

Ref. [21]

Glycerol

\( \Gamma_Q / Q^2 \) (meV/nm\(^2\))

\( \Gamma_Q / Q^2 \) (meV/nm\(^2\))

Temperature (K)

Temperature (K)

\( \Gamma_Q / Q^2 \) (meV/nm\(^2\))

\( \Gamma_Q / Q^2 \) (meV/nm\(^2\))
\[ \Gamma_0/Q^2 \text{ (meV/nm}^2) \]

\[ T \text{ (K)} \]

- \[ \text{SiO}_2 \] -

Ref. [13]
Ref. [11]
Ref. [25]
Ref. [24]
Ref. [2]