

Nondynamic Origin of the High-Frequency Acoustic Attenuation in Glasses

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The sound attenuation in the THz region is studied down to $T = 16$ K in glassy glycerol by inelastic x-ray scattering. At striking variance with the decrease found below ≈ 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 nondynamic origin of the attenuation of THz sound waves, and confirms a similar conclusion obtained in SiO₂ 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 regions, 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 [1]. This result is the outcome of extensive studies on the shape of $S(Q, E)$ performed using molecular dynamics (MD) simulations [2–5] and the newly developed inelastic x-ray scattering (IXS) technique [1,6–8]. In the IXS and MD Q range ($Q \approx 0.01$ – 0.04 nm⁻¹), in addition to 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 high Q values. The study of the mechanisms leading to this damping, and, therefore, the investigation of the sound waves attenuation at these Q values 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 Γ_Q which seems to show a Q^2 dependence [1]. Moreover, in all the IXS data reported so far, Γ_Q/Q^2 has a negligible temperature dependence in a wide temperature region ranging from values well below the glass transition temperature, T_g , up to the liquid phase [1]. At variance with this behavior, as well known, the linewidth of the excitations in the GHz region, measured by BLS, shows a relevant temperature dependence, which becomes particularly strong in the limit of very small temperatures [9–14]. This temperature dependence has motivated many theoretical studies, leading to different hypotheses on the frequency (or Q) evolution of the attenuation mechanisms [15].

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 *temperature independent* in the whole $0.1T_g$ to T_g region, whereas, in this same region, the BLS linewidth increases by more than a factor of 10. These two opposite 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 crossover 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 [16].

The experiment has been carried out at the new very high energy resolution IXS beam line ID28, at the European Synchrotron Radiation Facility. The incident x-ray beam is obtained by a Si(11 11 11) backscattering monochromator [17] and the scattered photons are collected by a spherical silicon crystal analyzer operating at the same reflection [18]. The monochromatic beam has an energy of $\approx 21\,748$ eV and an intensity of 2×10^8 photons/s. The total energy resolution of 1.5 meV full-width-half-maximum (FWHM) has been determined from elastic scattering measurements in a Plexiglas sample. The momentum transfer, $Q = 2k_0 \sin(\theta_s/2)$, with k_0 the wave vector of the incident photon and θ_s the scattering angle,

is selected between 2 and 4 nm⁻¹ by rotating a 7 m long analyzer 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 crystal disks, 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

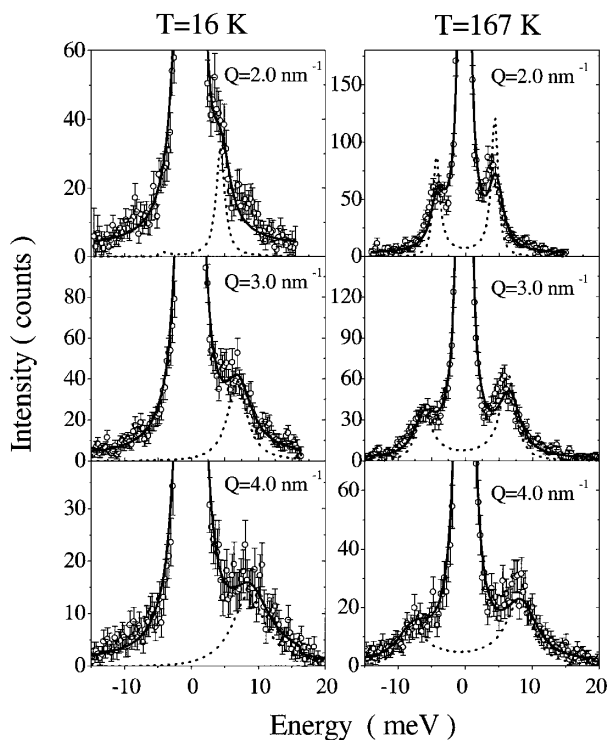


FIG. 1. Inelastic x-ray scattering spectrum of glycerol at $T = 16$ and 167 K and at the indicated Q values. The full lines are the best fit to the data as discussed in the text. The dotted lines represent the unconvoluted inelastic contributions to the fit.

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 α relaxation, observed in the liquid state and frozen in the glass, and of other relaxation processes with characteristic times slower than ≈ 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_0) and unrelaxed (c_∞) limiting values: $\Delta_Q^2(T) = Q^2(c_\infty^2 - c_0^2)$. 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 insensibility 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)

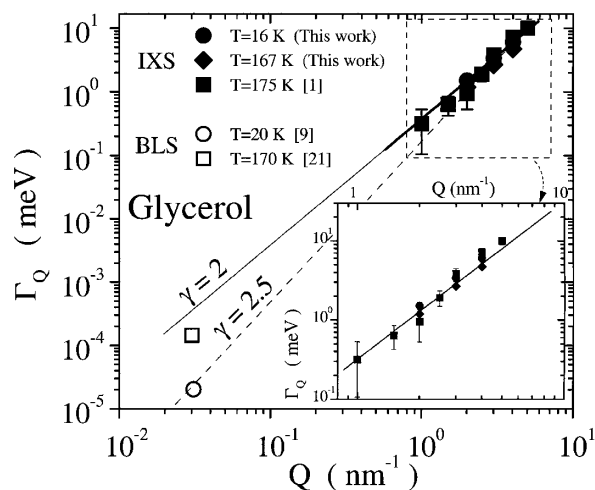


FIG. 2. The linewidth parameters Γ_Q for glycerol are reported as a function of Q at the indicated temperatures in the IXS (full symbols) and BLS (open symbols) Q regions. The inset shows an enlargement of the IXS Q region. The full line represents the Q^2 behavior, which is the best fit to Γ_Q at high Q . Also shown in the figure are the 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.

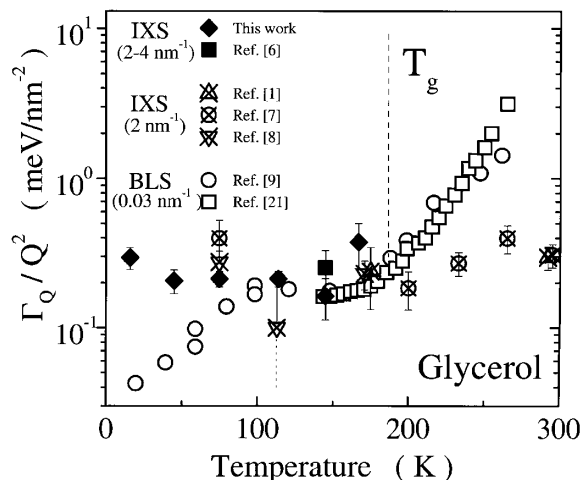


FIG. 3. Temperature dependence of Γ_Q/Q^2 in glycerol at $Q \approx 0.03 \text{ nm}^{-1}$ (open symbols), at $Q = 2 \text{ nm}^{-1}$ (crossed symbols) and averaged over the $Q = 2\text{--}4 \text{ nm}^{-1}$ region (full symbols). The vertical dashed line indicates the glass transition temperature, $T_g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

[9,21] and for Q in the IXS region. Here the crossed symbols refer to IXS measurements at fixed Q ($Q = 2 \text{ nm}^{-1}$) and the full symbols to the average of $\Gamma_Q(T)/Q^2$ over the $Q = 2\text{--}4 \text{ nm}^{-1}$ 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 $\approx 100 \text{ K}$, where it seems to reach a plateau. The further increase above T_g is due to the α relaxation; it is seen only 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, etc.) 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 [15]. In contrast to what 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 nonvanishing value of Γ_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 [16], who predict a $\Gamma_Q(T) \propto Q^2$ up to a Q_c value, above which $\Gamma_Q(T) = \text{const}$. In the case of amorphous silicon, Q_c has been calculated to be in the 0.1 nm^{-1} range [16].

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 $\nu_c \approx 100 \text{ GHz}$ frequency range. It is worth noting that a relaxation process with characteristic time $\tau = 1/2\pi\nu_c \approx 2 \text{ ps}$, and responsible for a linewidth of the order $\Gamma_Q/Q^2 \approx 0.2 \text{ meV/nm}^2$, should also give a dispersion of the sound velocity, $\delta c/c = \pi\Gamma_Q/Q^2\tau hc^2 \approx 1\%$, a value too small to be detectable with the accuracy achievable 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, $\Gamma_Q^{(S)} = DQ^2$, 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 $0.01\text{--}10 \text{ nm}^{-1}$ Q range. Under the hypothesis that $\Gamma_Q^{(S)} = Q^\gamma$, and assuming that at the lowest measured temperature $\Gamma_Q^{(S)} \equiv \Gamma_Q$, 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 γ 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 [2,5], and picosecond optical technique (POT) [26] data in another prototypical

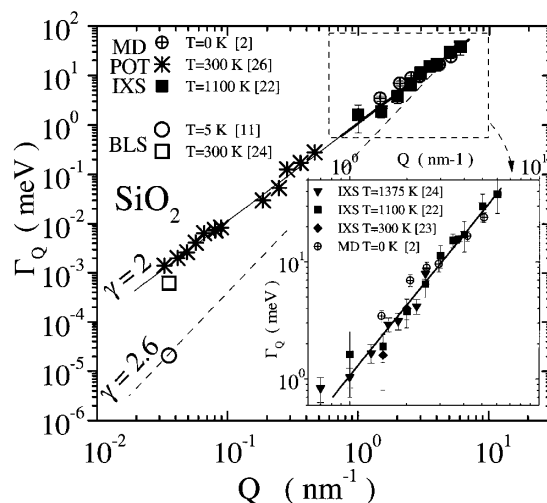


FIG. 4. Same as in Fig. 2 but for vitreous silica. Data from MD simulation (crossed symbols) and from POT (stars) are also reported. Here the low T BLS data indicate (if any) a power law with exponent $\gamma = 2.6$. The inset shows an enlargement of the high Q region.

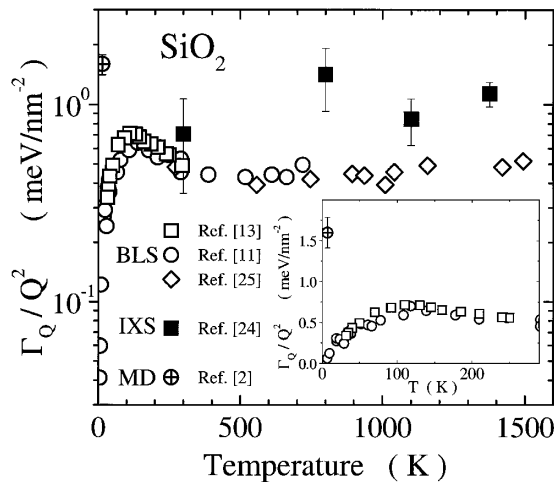


FIG. 5. Same as in Fig. 3 but for vitreous silica. The inset shows an enlargement of the low temperature region. The open circles refer to BLS data at $Q \approx 0.035$ (\square and \circ) and $Q \approx 0.025$ (\diamond) nm^{-1} , the full squares to IXS data at $Q = 1.6$ nm^{-1} , and the crossed circles to MD simulation in the harmonic ($T = 0$ K) limit. The inset shows an enlargement of the low T region.

glass: vitreous silica (ν - SiO_2). We report in Figs. 4 and 5 the $\Gamma_Q(T)$ values for ν - 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. This temperature region is further extended by an MD simulation performed in the harmonic approximation ($T = 0$) which 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 ν - SiO_2 data show a large T dependence. As in other glasses, also the high Q ν - SiO_2 data of Γ_Q have a Q dependence well represented by a Q^2 law (full line in Fig. 4). In ν - 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 ν - SiO_2 and glycerol allows one to formulate also for ν - SiO_2 the same hypotheses on the Q and T dependencies of $\Gamma_Q^{(D)}(T)$ and $\Gamma_Q^{(S)}$. It is worth noting, 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 ν - SiO_2 results clearly indicate 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 attenua-

tion 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 [15]. These findings imply a crossover 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 are consistent with a dynamic ($\Gamma_Q^{(D)}$) part that closely follows the one proposed by Fabian and Allen [16], 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 . Work is in progress in order to extend the study of the Q and T dependencies of Γ_Q in other glasses.

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