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High-frequency transverse dynamics in glasses

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Abstract

The improvement in performance of the inelastic x-ray scattering technique has led to accurate determination of the dynamic structure factors of glassy and liquid glycerol, in the region of exchanged momentum $Q = 2\text{--}23 \text{ nm}^{-1}$ and in the temperature range 80–570 K. Thanks to the improved statistical accuracy, it has been possible to identify, in the spectra at the lower temperatures, besides the propagating longitudinal mode, a second non- Q -dispersing peak at $\hbar\Omega_T \approx 8.5 \text{ meV}$. We interpret this peak as a signature of the transverse dynamics that, in topologically disordered systems, acquires a longitudinal symmetry component. This assignment is substantiated by the observation that this peak still survives, across the glass transition, in the liquid state, and vanishes when the structural relaxation time τ_α approaches Ω_T^{-1} : a behaviour consistent with the condition $\tau_\alpha\Omega_T \gg 1$ required for the existence of a non-relaxational transverse-like dynamics in the liquid state.

1. Introduction

The nature of the vibrational dynamics in topologically disordered systems at terahertz frequency is an issue not yet established due to the lack of translational symmetry and to the consequent impossibility of using a simple plane-wave description of the normal modes. The recent improvement of the inelastic x-ray scattering (IXS) technique has renewed the interest in this field, since it has allowed the experimental determination of the dynamic structure factor, $S(Q, \omega)$, over a wide kinematic region and, in particular, in the range of mesoscopic momentum transfer, Q . More specifically, it has been found that disordered materials support the propagation of sound waves in the terahertz frequency region, up to momentum transfer values close to the first maximum of the static structure factor, $S(Q)$ [1]. These acoustic-like collective excitations feel the effects of topological disorder, showing a Q -dependent broadening that turns out to be temperature independent [2]. These findings provided us with a picture for the vibrational modes in glasses which results in very good agreement with the different numerical works performed in the last years on this topic, i.e. molecular

dynamics and normal-mode analysis simulation of vibrational spectra [3–5]. Moreover, the experimental findings seem to be consistent with the scenario outlined by the recent extension of mode coupling theory calculations to the glassy phase [7].

Despite these successes in the study of sound propagation at terahertz frequencies in topologically disordered systems, the understanding of the high-frequency dynamics in glasses is still unsatisfactory. The above-mentioned numerical works, in fact, indicate a spectral feature that is still evading experimental observation: both theoretical calculations [7] and numerical simulations [4–6, 9] show, besides the peak associated with the longitudinal acoustic mode, the intriguing presence of a second excitation in $S(Q, \omega)$ or in the related longitudinal current spectra. This second excitation presents some general characteristics:

- (i) it appears in the spectra at Q -values larger than approximately one half the value of the first maximum of $S(Q)$;
- (ii) its energy position (Ω_T) is weakly Q -dependent, while its intensity increases with Q ;
- (iii) it has a ‘harmonic’ origin, as indicated by its presence in both MD and NMA simulations.

This feature has been suggested to indicate the existence of a transverse-like dynamics whose signature appears in longitudinal spectra due to microscopic disorder: the lack of homogeneity on these length scales could, indeed, lie at the origin of a phenomenon of ‘mixing’ between L and T dynamics. This phenomenon has been shown to survive also in the liquid state [9] provided that the condition $\tau_\alpha \Omega_T \gg 1$ is fulfilled (here τ_α is the structural relaxation time). The main evidence supporting a transverse-like nature of this second peak lies in the fact that it appears, at high Q -values, in both the transverse and the longitudinal spectra (though being much more intense in the former), having approximately the same more or less dispersing behaviour as the main peak of the other current [4, 6, 9]. All these convincing numerical results call for an experimental confirmation. It would, therefore, be of great interest to observe the behaviour of this transverse-like dynamics in the glassy state, at the glass transition, and, eventually, the conditions for its existence in the liquid state. In this work we report the experimental identification of this second excitation in the high-frequency dynamics of glycerol, an easily experimentally accessible prototype glass-forming system. Using IXS we find, besides the longitudinal mode, the presence in $S(Q, \omega)$ of a second excitation at $\hbar\Omega_T = E_T \simeq 8.5$ meV, showing up at wavevectors larger than 7 nm^{-1} with almost no Q -dispersion in energy. With increasing temperature this feature does not change energy but loses intensity, and progressively disappears in the tails of the central peak, becoming no longer observable above ≈ 500 K. At these high temperatures the width of the central peak of $S(Q, \omega)$, consistently with the extrapolation of the temperature dependence of the viscosity, indicates that the structural relaxation time, τ_α , approaches the inverse frequency of the second peak. This observation suggests that this secondary peak does reflect the transverse dynamics. Indeed, the transverse dynamics is fully relaxed in the liquid at high temperatures, and appears as a vibrational contribution on lowering the temperature, when the condition $\Omega_T \tau_\alpha(T) \gg 1$ is fulfilled [10].

2. The IXS experiment

The experiment has been carried out at the very high-resolution beam-lines ID16 and ID28 of the European Synchrotron Radiation Facility. The instruments each consist of a triple-axis spectrometer working in a fixed backscattering geometry: the beam produced by a source composed of two undulators is pre-monochromatized to a resolution of 10^{-4} by a double cryogenically cooled silicon crystal working on the (1, 1, 1) Bragg reflection and then is backscattered by the main silicon monochromator [11] at an angle of 89.98° in order to

maximize the angular acceptance at the necessary energy resolution: in this geometry, the loss of flux due to the intrinsic divergence of the beam is indeed minimized. Thanks to this optimization, high-order Bragg reflections can be used with a consistent residual flux: for this experiment the Si(11, 11, 11) configuration has been chosen: with an incident photon energy of 21748 eV, it gives an instrumental energy resolution of 1.6 meV (FWHM) and a flux of 7×10^8 photons on the sample with a 200 mA current in the storage ring. The beam is then focused on the sample by a toroidal mirror with a $100 \times 300 \mu\text{m}^2$ spot size. The momentum transfer is selected by a 7 m rotating analyser accordingly to the relation $Q = 2k_i \sin(\theta_s/2)$ where θ_s is the scattering angle. The scattered photons are then collected by a five-analyser system positioned at the end of the arm, with the analysers held next to each other with a constant angular offset equivalent to 3 nm^{-1} . Each analyser consists of a 'spherical' perfect crystal obtained by gluing $\approx 10\,000$ small perfect silicon crystals on a spherical surface [12] in order to maximize the collection of photons, according to the desired momentum resolution (0.4 nm^{-1}), by means of a focusing optics. Finally, the analysers backscatter the photons on a Peltier-cooled Si-diode detector. Due to the fixed geometry, the energy scans at constant Q are performed by varying the monochromator temperature with respect to that of the analyser crystals with millikelvin precision.

The system studied in this work is a sample of high-purity anhydrous glycerol ($\text{C}_3\text{H}_8\text{O}_3$) purchased from Aldrich. For the low-temperature measurements it was put in a 20 mm long Pyrex cylindrical cell closed by 1 mm thick diamond windows with a 4 mm opening. Due to the highly hydrophilic behaviour of glycerol, the cell was loaded inside an argon glove box and then placed in a closed-cycle cryostat. For the high-temperature experiment we used a 20 mm long nickel cylinder closed by two sapphire windows (1 mm thick, 8 mm in diameter) connected to the metal with a gold welding: the cylinder was filled through a Pyrex tube welded to the metal inside the glove box and then closed with the flame. The high temperatures were reached by heating the sample in a standard oven, working by means of an omega-shaped resistance operating in vacuum.

3. The low-temperature spectra: the presence of a second peak

The spectra at different temperatures were collected in three distinct experiments. In the first run we studied the Q -dependence ($Q = 2\text{--}15 \text{ nm}^{-1}$) at $T = 79 \text{ K}$. In the other runs, after a preliminary study that indicated $Q = 17 \text{ nm}^{-1}$ as the best-suited Q -value for following the temperature evolution of the secondary peak observed in the first run, we studied different temperatures ($T = 170, 300, 423, 563 \text{ K}$ in the second run and $T = 200, 343, 373, 473, 523 \text{ K}$ in the third) at $Q = 17 \text{ nm}^{-1}$. To enhance the statistics, the spectra of the second experiment were collected only on the Stokes side, including a small portion of the anti-Stokes side to cover most of the central peak.

The IXS data collected for the glycerol glass sample at $T = 79 \text{ K}$ are reported in figures 1 and 2. Besides an intense central curve, the spectra show a Q -dependent inelastic signal. In the low- Q region, figure 1, this is characterized by a single feature whose energy position and width increase with Q . This excitation is due to the propagating longitudinal acoustic modes, as already established in previous works [2, 13]. Thanks to the increased statistical accuracy with respect to previous experiments, one can now directly observe in the rough data that, at Q larger than 7 nm^{-1} (figure 2), a new weakly dispersing feature appears at $\approx 7\text{--}8 \text{ meV}$. This secondary peak is particularly evident in the spectra at the highest reported Q -values. To get quantitative information from the spectra, the data have been fitted by the convolution of the experimental resolution function with a model function, weighted by the detailed balance function to take care of quantum effects of the Bose–Einstein (BE) statistics (obviously very

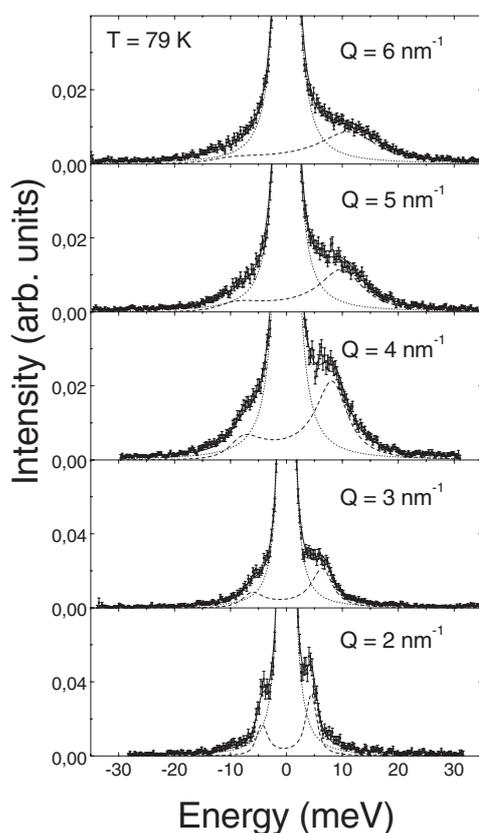


Figure 1. IXS spectra of glassy glycerol at $T = 79$ K for selected values of the exchanged wavevector (dots with error bars). We also show the total fitting result (full curve) which seems to be well reproduced by the sum of the measured experimental resolution for the elastic curve (dotted curve) and one purely inelastic contribution (dashed curve).

relevant at this temperature, as can be seen from the asymmetry of the inelastic signal). The model function is composed of:

- (1) a delta-function to account for the central line; at high temperature—where the broadening of the central peak becomes relevant—the delta-function is replaced by a Cole–Davidson (CD) function;
- (2) a damped harmonic oscillator (DHO) to account for the longitudinal mode;
- (3) a Lorentzian for the secondary peak, where its presence is statistically appreciable.

This model function has been chosen only to get information on the peak(s) position and broadening; a full description of the spectral shape would need a detailed generalized hydrodynamic model where the transverse and the longitudinal variables enter together into a generalized Langevin equation, a treatment which goes beyond the scope of the present work. The spectra have been fitted with and without the second Lorentzian in turn, and an F -test has been performed in order to establish whether the secondary peak is statistically necessary to describe the spectra or not. This latter turns out to be always the case for Q larger than 7 nm^{-1} . The fitting procedure always gives χ^2 -values within three σ_{χ^2} (about 200 fitted points and seven low- Q or ten high- Q fitting parameters; at high T a further parameter is needed for the stretching of the CD function). In all cases the relevant fitting parameters (peak positions)

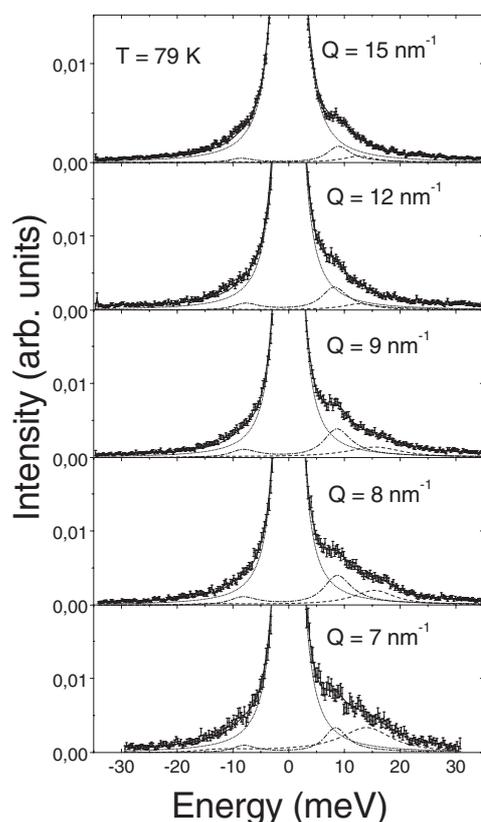


Figure 2. As figure 1, but for different Q -values. In this Q -range, one can appreciate that the inelastic signal needs the presence of a second contribution (dotted-dashed curve) in the fitting function to reproduce the spectrum lineshape well.

were found to be only slightly correlated with the other one (the maximum of the covariance matrix is ≈ 0.7). The chosen model represents the experimental data reasonably well, as shown in figures 1 and 2. In figure 3 we report the energy positions of the two features: the longitudinal acoustic mode (Ω_L) and the secondary peak (Ω_T). The slope of Ω_L consistently reproduces, in the low- Q linear dispersion region, the correct value of the velocity of sound ($v_L = 3600 \pm 30 \text{ m s}^{-1}$) and is in good agreement with previous IXS results and Brillouin light scattering data extrapolations. In the high- Q region we still observe a dispersion of Ω_L that, as expected, has a maximum at a Q -value approximately half-way from the maximum of $S(Q)$, and a minimum in the Q -region where $S(Q)$ attains its maximum. This dispersion of Ω_L is consistent with the concept of a pseudo-Brillouin zone in disordered systems, as discussed elsewhere [14]. The secondary peak is observed at the basically Q -independent energy $\hbar\Omega_T = 8.5 \pm 0.5 \text{ meV}$ (open circles in figure 3). Its intensity, as can be directly evinced from a more detailed analysis of the data in figure 2, shows an interesting Q -dependence: it increases with increasing Q . This may be due to various effects, among which are the expected Q^2 -dependence of the cross-section of a non-dispersing mode (localized or internal molecular mode), and/or the possible Q -dependence of the longitudinal versus transverse symmetry components of the eigenvectors associated with this mode. The investigation of these points is obviously crucial for the understanding of the origin of the secondary peak.

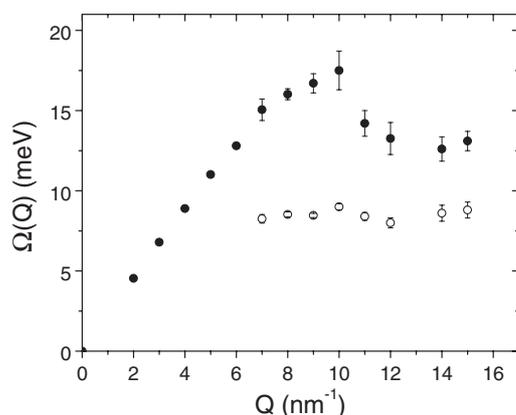


Figure 3. Energy positions of the longitudinal (full dots) and transverse (open dots) acoustic modes at $T = 79$ K, as determined by the fitting procedure described in the text.

4. The transverse nature of the second peak: a temperature study

Aiming to establish the origin of the observed secondary peak, we studied this feature as a function of temperature in order to investigate its evolution across the liquid–glass transition ($T_g \approx 180$ K) and up to the normal liquid phase. This temperature dependence has been studied at $Q = 17 \text{ nm}^{-1}$ from $T = 170$ K (in the glassy phase) to 570 K. The Stokes sides of the spectra at selected temperatures are reported in figure 4 and, on a logarithmic scale, in figure 5.

As can be seen in the inset of figure 4, at $Q = 17 \text{ nm}^{-1}$ the contribution coming from the longitudinal mode is negligible. From figures 4 and 5 one clearly observes that both the quasi-elastic and the secondary-peak spectral features show a striking T -dependence: on increasing T , the central curve gets increasingly broader and the secondary peak is already hardly visible at ≈ 350 K. As long as the secondary peak is statistically significant, we find that its energy position and width are T -independent, while its intensity decreases. The fits to the data provide a quantitative description of these behaviours, and, as reported in figure 6, the ratio of the integrated intensities of the secondary peak to the central peak sharply decreases at high temperatures.

This behaviour is opposite to the increase that one would normally expect if the secondary peak were associated with an intramolecular vibration. Indeed:

- (i) on increasing T , the central peak intensity is expected to slightly decrease, following the Debye–Waller T -dependence;
- (ii) the secondary-peak intensity is expected to increase following the BE statistics.

To further emphasize the statistical significance of the secondary-peak intensity behaviour, and to show that this feature is not simply lost in the tails of the increasingly broader central peak, we report in figure 7 at $T = 563$ K the simulation (dashed curve) of how the spectrum should look under the following assumptions:

- (i) a central line with a constant integrated intensity (the same as for the spectrum at $T = 170$ K) and the observed width;
- (ii) a secondary peak obtained from the glass spectrum at $T = 170$ K, keeping the energy position and width constant, and increasing the integrated intensity according to the BE statistics.

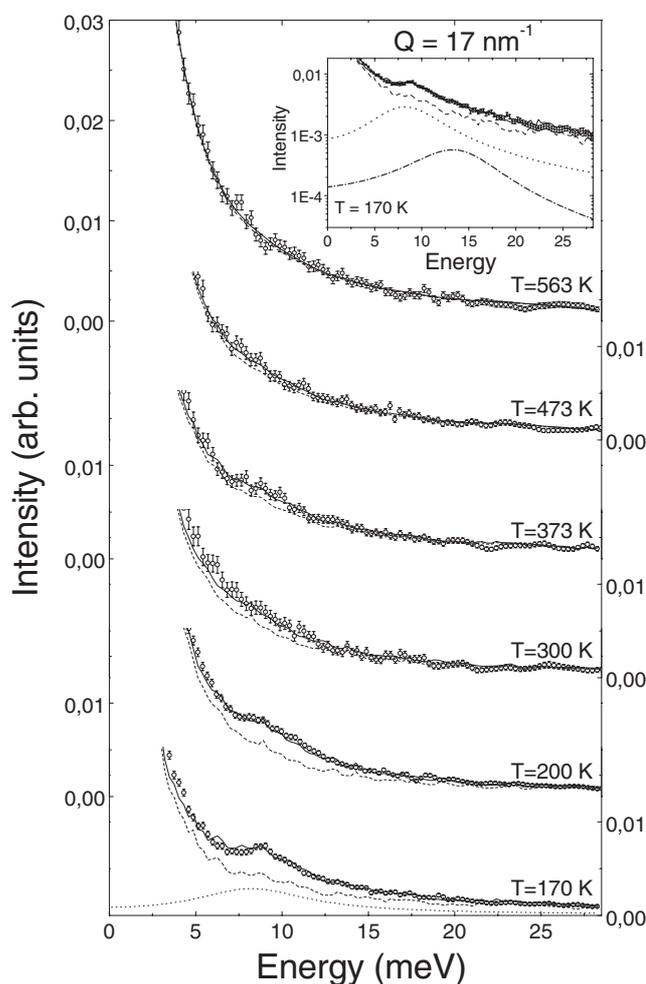


Figure 4. The Stokes sides of the IXS spectra of glycerol at the Q -value investigated ($Q = 17 \text{ nm}^{-1}$) for selected temperatures (open dots with error bars). The full curve represents the best fits to the data and the dashed curve the contribution of the central peak only. For $T = 170 \text{ K}$ we also evidence the inelastic signal for the secondary peak (dotted curve). In the inset the negligible contribution of the longitudinal excitation (dot-dashed curve) is shown, on a logarithmic scale.

This simulation underlines the observed disappearance of the secondary peak at high T beyond any statistical uncertainty. The temperature dependence of the secondary peak allows us, therefore, to exclude on general grounds the possibility that this excitation is due to an internal molecular mode. Indeed, if this were the case, one should expect a behaviour giving rise to the simulated spectrum in figure 7. Finally, it is important to underline that, as can be seen from figure 5, the broadening of the quasi-elastic line, which appears in the high-temperature spectra, is a manifestation of the rapid decreasing of the structural relaxation time. On the basis of the reported results, we propose that the secondary peak is due to the transverse-like acoustic dynamics in a topologically disordered structure. In fact, in the glycerol glass, two excitation branches are present, as shown in figure 3. This result is very similar to those obtained in MD simulations of other systems, where indeed these two excitations have been

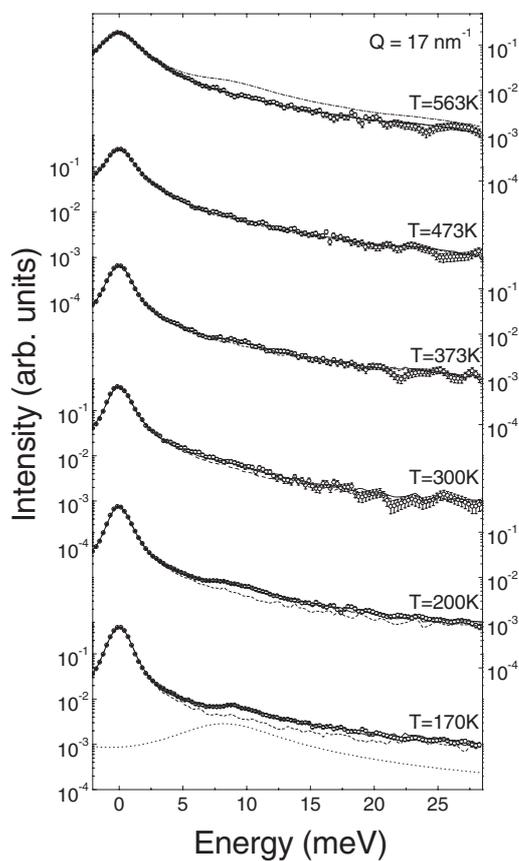


Figure 5. As figure 4, but on a logarithmic scale, to better emphasize the broadening of the central peak above T_g .

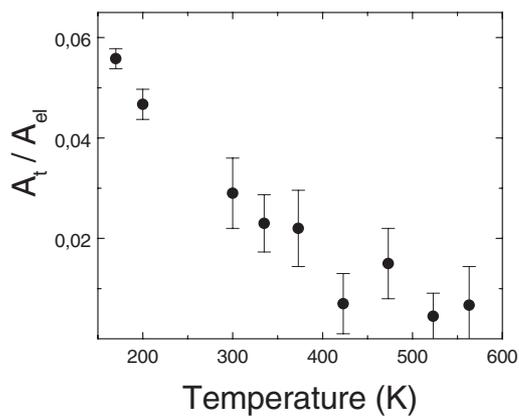


Figure 6. This figure shows the rapid decrease of the integrated intensity ratio of the secondary peak to the central peak as obtained from fit results.

assigned, respectively, to the acoustic longitudinal-like and to the transverse-like dynamics on the basis of the analysis of calculated longitudinal and transverse current spectra [6, 9]. This

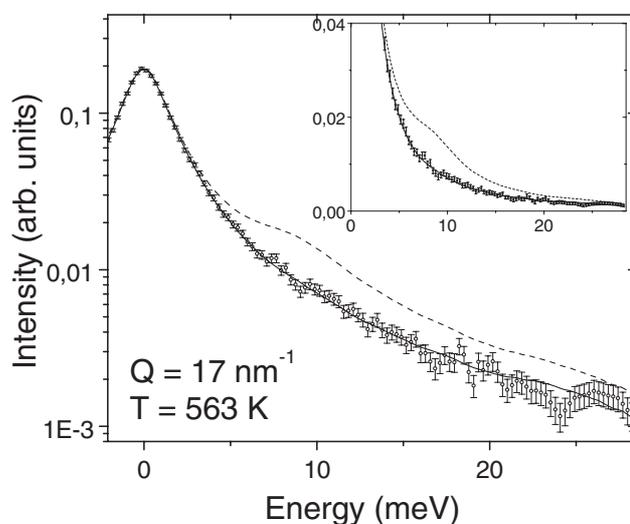


Figure 7. This figure shows, on logarithmic and linear (inset) scales, the spectrum at $T = 563$ K, already reported in previous figures, showing how it would appear if the secondary peak were related to some intramolecular mode, under the assumptions explained in the text.

assignment is also consistent with the observation that the secondary-peak intensity increases with increasing Q . Indeed, on decreasing the length scale, the local disorder forbids more and more the pure polarization of the eigenvectors, thus leading to the mixing of the longitudinal and transverse symmetries. Clearly, due to this mixing, the longitudinal part of the transverse-like excitation spills out in $S(Q, \omega)$. This interpretation of the origin of the secondary peak is additionally supported by the behaviour observed in the liquid phase. Indeed, a vibrational transverse-like dynamics in the liquid state can only be active when the structural relaxation time is much longer than the transverse vibration period (elastic limit), i.e. when the local structure is frozen for a long enough time that a shear stress does not decay through relaxational processes. Conversely, in liquids at high temperature, where the condition $\Omega_T \tau_\alpha \gg 1$ no longer holds, the vibrational transverse dynamics switches off and the secondary peak disappears. It is important to point out that this behaviour is distinctly different from that of the longitudinal acoustic excitations. Indeed—as experimentally observed—these latter exhibit a vibrational nature regardless of the value of $\Omega_L \tau_\alpha$, which only drives the magnitude of the sound velocity and absorption.

5. Conclusions

In conclusion, in this work, we have reported the experimental evidence for the existence of a second non- Q -dispersing excitation, besides the longitudinal mode, in glassy and liquid glycerol at terahertz frequencies. This second peak turns out to show a behaviour in qualitative agreement with the predictions of numerical simulations [4–6, 9, 17]. As suggested by MD and NMA simulations, we have assigned a transverse-like origin for this feature. The robustness of this assignment is proved by a temperature study which has shown the behaviour of an acoustic transverse collective mode. It is tempting to suggest that the origin of the boson peak in glycerol (the excess in the vibrational density of states as derived from specific heat measurements and as observed in the *incoherent* scattering function [18]) could be found

in the non-dispersing transverse acoustic branch. The proof of the existence of a relation between a flat T branch and the boson peak has been recently reached for vitreous silica by MD simulations [6]. Therefore, we expect the scenario observed here to be a general property of disordered matter, not limited to the specific case of glycerol. Indications in this direction come not only from MD simulations [6, 9], but also from experimental data on glassy SiO₂ and liquid water [8, 17].

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