

High-frequency transverse-like excitations in glassy glycerol

TULLIO SCOPIGNO^{†§}, EMANUELE PONTECORVO[†],

ROBERTO DI LEONARDO[†], MICHAEL KRISCH[‡], GIULIO MONACO[‡],
GIANCARLO RUOCCO[†], BARBARA RUZICKA[†] and FRANCESCO SETTE[‡]

[†]Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia,
Università di Roma La Sapienza, 00185 Roma, Italy

[‡]European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France

ABSTRACT

The dynamic structure factor of glassy and liquid glycerol has been measured by inelastic X-ray scattering in the exchanged momentum Q region $Q=2\text{--}23\text{ nm}^{-1}$ and in the temperature range 80–570 K. Besides the propagating longitudinal mode, at low temperatures the spectra show a second non- Q -dispersing peak at $\hbar\Omega_T \approx 8.5\text{ meV}$. This peak is the signature of the *transverse* dynamics which, in topologically disordered systems, acquire a small Q -dependent longitudinal symmetry component. This assignment is substantiated by a study of the temperature dependence of the intensity of the second peak. This study showed that, in the liquid, the second peak intensity 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.

The understanding of high-frequency dynamics in the glassy state has recently made progress because of the development of the inelastic x-ray scattering (IXS) technique, which allows one to measure the dynamic structure factor $S(Q, \omega)$ in the mesoscopic momentum transfer Q range. This advance established the presence of longitudinal-acoustic-like excitations (Sette *et al.* 1998, Pilla *et al.* 2000) in topologically disordered systems. These excitations exist up to momentum transfer values close to the first maximum of the static structure factor $S(Q)$ and have a characteristic Q -dependent broadening related to the topological disorder (Ruocco *et al.* 1999). These results confirmed earlier predictions of different molecular dynamics (MD) and normal mode analysis (NMA) simulation studies of disordered systems (Taraskin and Elliott 1997a, b, Dell'Anna *et al.* 1998, Ribeiro *et al.* 1998a, b, Feldman *et al.* 1999, Horbach *et al.* 2001). They are also consistent with a recent extension of the mode-coupling theory to the glassy phase (Goetze and Mayr 2000).

Despite these successes on the study of sound propagation at terahertz frequencies in topologically disordered systems, a satisfactory understanding of the high-frequency *transverse* dynamics in glasses is still missing. Interestingly, besides the peaks associated with sound modes, theoretical and numerical studies also predicted a second excitation in the $S(Q, \omega)$ or in the related longitudinal current spectra

§ Author for correspondence. Email: tullio.scopigno@phys.uniroma1.it.

(Sette *et al.* 1996, Sampoli *et al.* 1997, Goetze and Mayr 2000). This feature has been suggested to indicate the existence of a transverse-like dynamics in disordered systems, and it has been seen to survive also in the liquid state (Sampoli *et al.* 1997). The main reason supporting the 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 although being much more intense in the former. Other general characteristics of this second excitation are as follows.

- (i) It appears in the spectra at Q values larger than approximately half the value of the first maximum of the $S(Q)$.
- (ii) It shows a weakly Q -dispersing behaviour.
- (iii) It has a 'harmonic' origin, as pointed out by its presence in both MD and NMA simulations.

In spite of these convincing numerical results, the firm experimental observation of this feature in glasses is still missing. It would be, therefore, of great interest to understand the behaviour of these transverse dynamics in the glassy state, at the glass transition, and eventually the conditions for its existence in the liquid state.

This paper is dedicated to 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 report the presence in the $S(Q, \omega)$ of a second excitation at $\hbar\Omega_T = E_T \approx 8.5$ meV, appearing beside the longitudinal mode at wave vectors larger than 7 nm^{-1} with almost no Q dispersion. With increasing temperature this feature does not change energy and progressively disappears in the tails of the central peak, becoming no longer observable above about 500 K. At these high temperatures the width of the central peak of the $S(Q, \omega)$, 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 (SP) does reflect the transverse dynamics. Indeed, the transverse dynamics are fully relaxed in the liquid at high temperatures and appear as a vibrational contribution on lowering the temperature, when the condition $\Omega_T \tau_\alpha(T) \gg 1$ is fulfilled (Boon and Yip 1980).

The experiment has been carried out at the very-high-resolution beam lines ID16 and ID28 of the European Synchrotron Radiation Facility. The instruments consist of a back-scattering monochromator and five independent analyser systems, next to each other with a constant angular offset on an analyser arm 7 m long. The utilized Si(11, 11, 11) configuration, with an incident photon energy of 21748 keV, gives an instrumental energy resolution of 1.6 meV (full width at half-maximum) and an offset of 3 nm^{-1} between two neighbouring analysers. The momentum transfer is selected by rotating the analyser arm. The energy scans at constant Q were performed by varying the monochromator temperature with respect to that of the analyser crystals. For the low-temperature measurements the glycerol sample, high-purity anhydrous $\text{C}_3\text{O}_3\text{H}_8$, was put in a Pyrex cylindrical cell 20 mm long closed by diamond windows 1 mm thick with a 4 mm opening. The cell was loaded inside an argon glove box and then placed in a closed-cycle cryostat. The high-temperatures measurements were performed by loading a nickel cylinder 20 mm long closed by two sapphire windows (1 mm thick and 8 mm in diameter) and heated in a standard oven operated in vacuum. 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 $T = 79$ K. In the other runs, after a preliminary study that

indicated $Q = 17 \text{ nm}^{-1}$ as the most suitable Q value to follow the temperature evolution of the secondary peak observed in the first run, we studied different temperatures ($T = 170, 300, 423$ and 563 K in the second run and $T = 200, 343, 373, 473$ and 523 K in the third run) at $Q = 17 \text{ nm}^{-1}$. To increase the statistics the spectra of the second experiment were collected only on the Stokes side, including only a small portion of the anti-Stokes data to cover most of the central peak.

The IXS data collected on the glycerol glass sample at $T = 79 \text{ K}$ are reported in figure 1. Besides an intense central line, the spectra show a Q -dependent inelastic signal. In the low- Q region, this is characterized by a single feature whose energy position and width increase with increasing Q . This excitation is due to the propagating longitudinal acoustic modes, as already established in previous work (Masciovecchio *et al.* 1996, Ruocco *et al.* 1999). Because of the increased statistical accuracy with respect to previous experiments, one can now observe directly in the raw data that, at Q larger than 7 nm^{-1} , a new weakly dispersing feature appears at about 7–8 meV. This SP, shown in the right-hand column of figure 1, is particularly evident in the spectra at the highest reported Q values.

To obtain 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. The model function is composed of, firstly, a delta function to account for the central line (at high temperatures, where the broadening of the central peak becomes relevant, the delta function is substituted by a Cole–Davidson function), secondly, a damped harmonic oscillator for the longitudinal mode and, thirdly, when necessary, a Lorentzian for the SP. This model function has been chosen only to obtain information on the peak position(s) and broadening, a full description of the spectral shape would need a detailed generalized hydrodynamic model where both the transverse and the longitudinal variables are considered. The spectra were fitted with and without the second Lorentzian, and the F test has been applied to the result in order to establish whether the SP is statistically necessary to describe the spectra. This is always the case for Q larger than 7 nm^{-1} . The chosen model represents the experimental data well, as shown in figure 1.†

In figure 2 we report the energy positions of the two features: for the longitudinal acoustic mode, Ω_L and, for the SP, Ω_T . The slope of Ω_L consistently reproduces, in the low- Q linear dispersion region, the correct value of the velocity of sound ($v_L = 3600 \pm 30 \text{ m s}^{-1}$). 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 the $S(Q)$, and a minimum in the Q region where the $S(Q)$ has a maximum. This dispersion of Ω_L is consistent with the concept of a pseudo-Brillouin zone in disordered systems, as discussed elsewhere (Scopigno *et al.* 2001).

The SP is observed at the essentially Q -independent energy $\hbar\Omega_T = 8.5 \pm 0.5 \text{ meV}$. This feature, as can be directly demonstrated from a more detailed analysis of the data in figure 1, shows an interesting Q dependence in its intensity, which increases with increasing Q . This may be due to various effects, among which the expected Q^2

† 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 temperatures a further parameter is needed for the stretching of the Cole–Davidson function). In all cases the relevant fitting parameters (peaks positions) were found to be only slightly correlated with the other (maximum of the covariance matrix, about 0.7).

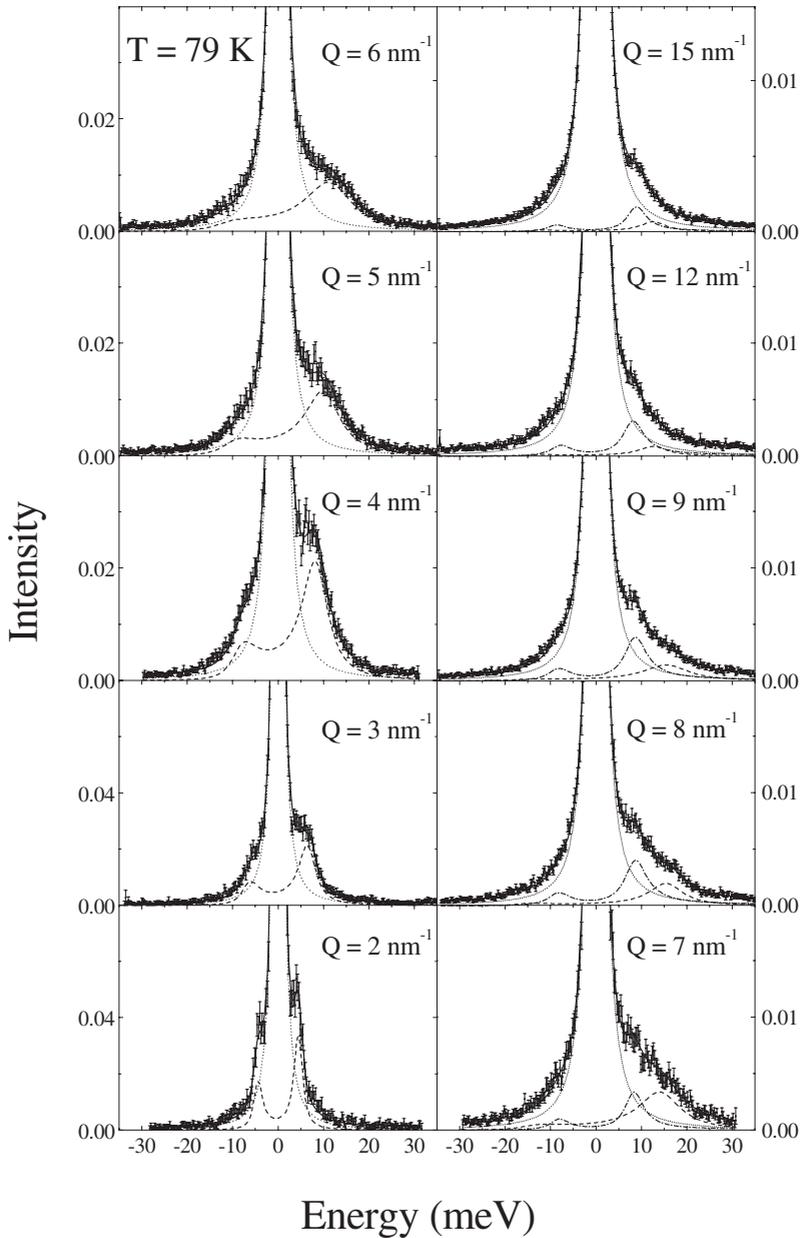


Figure 1. IXS spectra of glassy glycerol at $T=79$ K for selected values of the exchanged wave vector (\bullet). The total fitting result (—) is also reported, together with the genuine inelastic signal relative to the longitudinal mode (---). Above $Q \gtrsim 6$ nm $^{-1}$ (right-hand column) we included a second inelastic contribution in the fitting function (-·-). The measured instrumental resolution function is also shown (· · · · ·).

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 to this mode. Investigation of these points is obviously crucial to the understanding of the origin

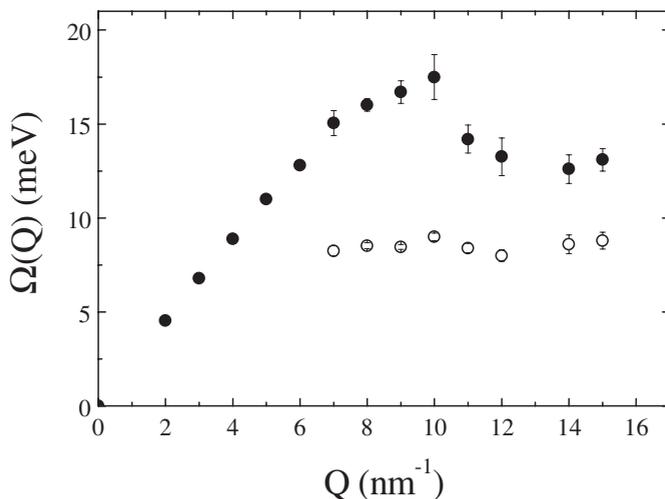


Figure 2. Energy position of the longitudinal (●) and transverse (○) acoustic modes at $T = 79$ K, as determined by the fitting procedure described in the text.

of the SP. For this purpose we studied this feature as a function of temperature in order to investigate its evolution across the liquid-to-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 $T = 570$ K. The Stokes side of the spectra at selected temperatures is reported in figure 3.

As can be seen in figure 4, at $Q = 17 \text{ nm}^{-1}$ the contribution coming from the longitudinal mode is negligible, and both the quasielastic and the SP spectral features show striking temperature dependences; on increasing the temperature the central line becomes increasingly broader and the SP becomes hardly visible already at about 350 K. As long as the SP is statistically significant we find that its energy position and width are temperature independent, while its intensity decreases. The fits to the data provide a quantitative description of these behaviours, and, as reported in the inset of figure 3, the ratio of the integrated intensity of the SP to that of the central peak sharply decreases at high temperatures. As shown in figure 4, this behaviour is opposite to the increase that one would normally expect. Indeed, firstly, the central peak intensity should slightly decrease, following the Debye–Waller temperature dependence and, secondly, the SP intensity should increase following the Bose–Einstein statistics.

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

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

This simulation emphasizes the observed disappearance of the SP at high temperatures beyond any statistical uncertainty. The temperature dependence of the SP

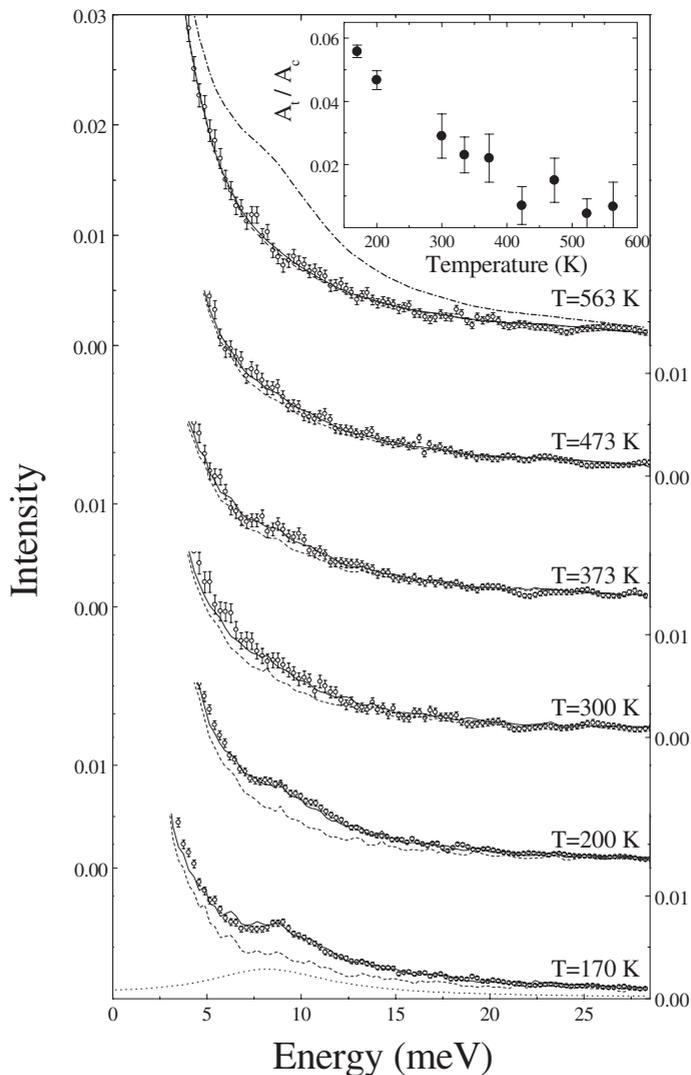


Figure 3. Stokes side of the IXS spectra of glycerol at $Q = 17 \text{ nm}^{-1}$ for selected temperatures (\odot). Also reported are the best fits to the data (—) and the central peak contribution (---). For $T = 170 \text{ K}$ we also report the inelastic signal for the SP (\cdots). At $T = 563 \text{ K}$ we also show how the spectrum should appear if the SP were related to some intramolecular mode. In the inset we report the ratio of the inelastic (SP mode) to elastic intensity as determined by the fit.

allows us, therefore, to exclude on general grounds 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 shown as the uppermost curve in figure 3.

Finally, the broadening of the quasielastic line which appears in the high-temperature spectra is quantified in figure 5, where we report the structural relaxation time as obtained from the Cole–Davidson contribution to the utilized fitting function. These values are in good agreement with light scattering and viscosity data

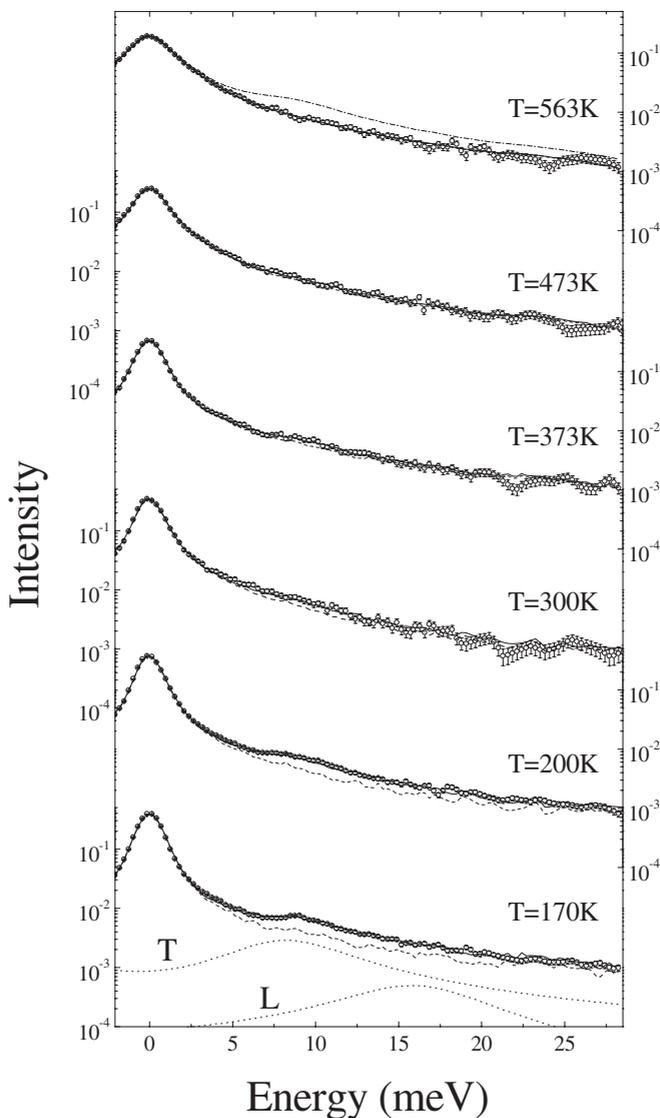


Figure 4. Same as figure 3 but on a logarithmic scale, to emphasize the broadening of the central peak above T_g better. The contribution from the longitudinal mode for $T = 170$ K is also reported.

(Landolt–Bornstein 1965, Paolucci and Nelson 2000), testifying the reliability of the whole presented data analysis.

On the basis of the reported results, we propose that the SP is due to the transverse-acoustic-like dynamics in a topologically disordered structure. In fact, in the glycerol glass two excitation branches are present, as shown in figure 2. This result is very similar to those obtained in MD simulations, where indeed these two excitations have been assigned respectively to the longitudinal-acoustic-like and to the transverse-acoustic-like dynamics on the basis of the analysis of calculated longitudinal and transverse current spectra (Sampoli *et al.* 1997, Pilla *et al.* 2002). This assignment is also consistent with the observation that the SP

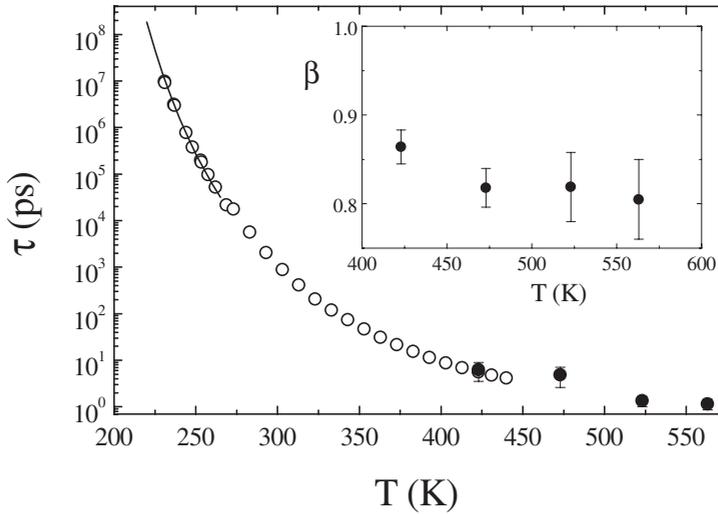


Figure 5. Values of the structural relaxation time in glycerol as a function of temperature: (●), this work (central peak broadening); (—), light scattering; (○), viscosity data scaled by an arbitrary factor. The inset shows the values of the stretching exponent of the Cole–Davidson function.

intensity increases with increasing Q . Indeed, on decreasing the length scale, the local disorder increasingly forbids the pure polarization of the eigenvectors, thus leading to mixing of longitudinal and transverse symmetries. Clearly, it is exactly because of this mixing that the longitudinal part of the transverse-like excitation appears in the $S(Q, \omega)$. This interpretation of the origin of the SP is additionally supported by the behaviour observed in the liquid phase. Indeed, a vibrational transverse-like dynamics in the liquid state can only be supported when the structural relaxation time is much longer than the transverse vibration period (elastic limit), that is 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 temperatures, where the condition $\Omega_T \tau_\alpha \gg 1$ is no longer fulfilled, the vibrational transverse dynamics are no longer allowed (Boon and Yip 1980) and the SP disappears. It is important to point out that this behaviour is distinctly different from that of the longitudinal acoustic excitations. In fact, as experimentally observed, the latter keep their vibrational nature independently of the value of $\Omega_L \tau_\alpha$, which only affects the value of the sound velocity and absorption.

In conclusion, we report the first experimental evidences of the existence of transverse-like dynamics in glasses and liquids glycerol at terahertz frequencies. These dynamics give rise to a well-defined and *non-Q*-dispersing excitation. 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 (Wuttke *et al.* 1994, 1995, Bermejo *et al.* 1996, Dawidowski *et al.* 1996, Cuello *et al.* 1998)) could be found in the non-dispersing transverse acoustic branch. The proof of the existence of a relation between a flat-temperature branch and the boson peak has been reached recently for vitreous silica by MD simulations (Pilla *et al.* 2002). Therefore, we expect that the scenario observed here is a general property of disordered matter

and is not limited to the specific glycerol case. Indications in this direction come not only from MD simulations (Sampoli *et al.* 1997, Pilla *et al.* 2002) but also from experimental data on glassy SiO₂ and liquid water (Sette *et al.* 1996, Ruocco *et al.* 2001).

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