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Evidence of anomalous dispersion of the generalized sound velocity in glasses

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The dynamic structure factor $S(Q,\omega)$, of *vitreous silica*, has been measured by inelastic x-ray scattering in the exchanged wave-vector (Q) region $Q=4-16.5\ \mathrm{nm}^{-1}$ and up to energies $\hbar\omega=115$ meV in the Stokes side. The unprecedented statistical accuracy in such an extended energy range allows us to accurately determine the longitudinal current spectra and the energies of the vibrational excitations. The simultaneous observation of two excitations in the acoustic region and the persistence of propagating sound waves up to Q values comparable with the (pseudo-)Brillouin-zone edge allow us to observe a positive dispersion in the generalized sound velocity that, around $Q\approx 5\ \mathrm{nm}^{-1}$, varies from ≈ 6500 to ≈ 9000 m/s; this phenomenon was never experimentally observed in a glass.

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The stimulating evidence of the existence of short-wavelength phononlike excitations sustained by nonperiodic solids, as demonstrated by recent inelastic x-ray scattering (IXS) studies,[1] has motivated a massive number of investigations. This notwithstanding, a general consensus on the *characteristics* of observed excitations is still lacking.[2] Among several specific questions waiting for an answer, one of the most important is regarding the existence and the features of the *dispersion relations* in the whole first pseudo-Brillouin-Zone, and their connection with the well-known universal anomalies of glasses (low-temperature transport and thermodynamic properties,[3] excess in the density of states,[4] etc.).

In the specific case of vitreous silica, the archetype of the strong glasses, up to now the experimental studies were limited to (i) the low-Q region ($Q<4\ \mathrm{nm}^{-1}$)—investigated by IXS—where the spectra are described by a single excitation with energy position $[\hbar\Omega(Q)]$ linearly dispersing with Q,[5–7] and (ii) the high-Q region ($Q\geqslant 15\ \mathrm{nm}^{-1}$) where inelastic neutron scattering (INS) data [confined to the high-Q and low-ω portion of the $S(Q,\omega)$ due to the kinematic restrictions] show again spectra dominated by a single excitation, but having now a Q independent energy.[4,8] This scenario led to us the conclusion that the longitudinal acoustic branch in vitreous silica—dispersing with a sound velocity $v\approx 6400$ m/s at low Q—flattens at increasing Q giving origin to the boson peak.[9] However, as the crossover between the low-$[\Omega(Q)=vQ]$ and high-Q $[\Omega(Q)=\Omega_{BP}]$ regimes lies in the not-explored Q region, it was not possible to establish a firm conclusion on the shape of the dispersion relation of this mode. A hint on this issue came from molecular dynamic (MD) simulations. Surprisingly, the MD works showed the simultaneous presence of two excitations in the longitudinal current spectra at large enough Q ($Q>5\ \mathrm{nm}^{-1}$).[10–13] MD indicated that the excitation detected at low Q by IXS corresponds to the longitudinal acoustic (LA) mode, while that detected at high Q by INS is associated with the spilling of the transverse acoustic (TA) mode in the longitudinal spectra and not to the longitudinal branch.[13] The presence of the signature of the transverse dynamics in the *longitudinal* spectra is not surprising. Indeed, in a disordered medium, the polarization character of the modes becomes ill defined at short wavelengths—when the sound waves no longer see the system as a continuum—and this gives rise to modes with mixed polarization.[14]

The MD works[11–13] also indicated the presence, in vitreous silica, of another important feature of the LA branch: a positive dispersion of the generalized sound velocity, $v(Q)=\Omega(Q)/Q$. A positive dispersion of $v(Q)$ is usually observed in viscoelastic liquids where a steplike change of $v(Q)$ is found when the condition $\Omega(Q)\tau_\alpha(Q,T)=1$ is fulfilled, $\tau_\alpha(Q,T)$ being the structural (α) relaxation time. This condition marks the transition from the low-frequency (and low v) viscous behavior to the high-frequency (and high v) elastic behavior of the liquid. In glasses, $\tau_\alpha(Q,T)$ being basically *infinite*, the MD observed positive dispersion cannot be associated to the structural relaxation process but to a further relaxation process named *instantaneous* or *microscopic*. This process, already observed in the MD simulation of monatomic glasses[15] and, experimentally, in liquid metals above melting,[16] has been so far explained in term of *structural disorder*.[15] No experimental evidences for such a positive dispersion in glasses have been reported yet.

In this communication we present an IXS study of the dynamic structure factor of vitreous silica in the intermediate Q region ($4<Q<16.5\ \mathrm{nm}^{-1}$). Using also existing IXS data at $Q<4\ \mathrm{nm}^{-1}$, we draw a self-consistent picture of the whole pattern of excitations in the first pseudo-Brillouin-zone (p-BZ) of this prototype glass. Specifically, we find the following.

(i) The LA branch spans energies as high as 80 meV, confirming and extending the validity of previous IXS studies[5–7] limited to $Q<4\ \mathrm{nm}^{-1}$ and to $E<20$ meV;

(ii) Above $Q=4\ \mathrm{nm}^{-1}$ the spectra show the simultaneous presence of *two* excitations, the high energy one associated to the LA modes, and the low-energy one assigned to the TA excitation. The latter excitation appears in the longitudinal spectra due to the mixing phenomenon,[14] and its experimental observation confirms previous MD resultss[10–13] and parallels similar findings in glassy glycerol.[17]

(iii) Finally, and most importantly, the clear identification of longitudinal acoustic branch us allows to observe experimentally the existence in glasses of a positive dispersion of the generalized longitudinal sound velocity. The transition is found at $Q \approx 5$ nm^{-1}, where v undergoes a change from ≈ 6400 to ≈ 9000 m/s.

The measurements were performed in two different sessions at the inelastic x-ray scattering beam line ID16 of the European Synchrotron Radiation Facility. The experimental setup consists of a backscattering operating monochromator and of a 6.5 m analyzer arm hosting a five-analyzer bench with a constant angular offset between each analyzer. The incident energy was 17794 eV, corresponding to the Si(9,9,9) reflection. In this configuration the overall (full width at half maximum) energy and Q resolutions were $\delta E = 3.0$ meV and $\delta Q = 0.27$ nm^{-1}, respectively. The exchanged wave vector is selected by rotating the analyzer arm. Each energy scan was performed at constant momentum transfer by varying the relative temperatures of the monochromator and the analyzer crystals. Further details on the beamline are reported elsewhere.[18] The sample of vitreous silica (SUPRASIL), heated at $T = 1270$ K, was studied in a Q range not covered by previous measurements, i.e., at $Q = 4,5,6$ in a first run and from 6.5 to 16.5 nm^{-1} in step of 2.5 nm^{-1} in a second run. In order to follow the evolution of the inelastic signal, in the second run we performed wide energy scans up to 115 meV. To achieve the necessary statistical accuracy the spectra were collected on the Stokes side only (and on a small portion of the anti-Stokes to cover most of the central peak): the total integration time was 30 min/point, i.e., ≈ 120 hours for the collection of a whole spectrum.

As an example, the spectra obtained for three selected Q values are shown in Fig. 1. The IXS signal (open circles), proportional to the dynamic structure factor $S(Q,\omega)$, convoluted with the experimentally determined instrumental resolution function $R(\omega)$, is reported in log scale together with the elastic [dotted line, coincident with $R(\omega)$] and inelastic (dashed line) contributions as derived from the fit (see below). Directly from the IXS data—at least for the lowest two reported Q values—one can infer the presence of two shoulders, which are not present in the smoothly decreasing resolution function. These shoulders, indicated in the figure by arrows, point out the presence of two excitations. To get quantitative information on the energies of the excitations and on their Q dependences, the data have been fitted by the convolution of $R(\omega)$ with a model function for $S(Q,\omega)$ weighted by the detailed balance function. The model function is the sum of an elastic and an inelastic contribution, $S(Q,\omega) = S_{el}(Q,\omega) + S_{inel}(Q,\omega)$; the former, accounting for the frozen structural relaxation, is represented by a δ function and the latter has been tentatively described by one or two excitation(s) model through, respectively, one or two damped harmonic-oscillator function(s). This model function has been chosen only to extract information on the position of the peaks. Indeed, a full description of the spectral shape in the investigated Q region would need a detailed generalized hydrodynamic model, where the transverse and the longitudinal variables couple each other due to the broken ergodicity in the glass. The use of this detailed model to describe the spectra goes beyond the aim of the present Communication.

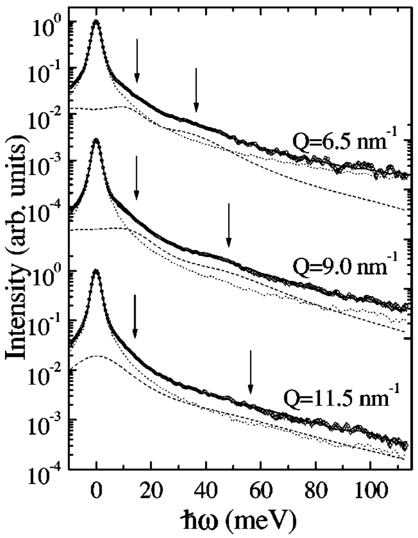

FIG. 1. IXS spectra of vitreous silica at $T = 1270$ K for selected values of the exchanged wave vector in the region of interest (open circles with error bars). The total fitting result with two excitations (full line) is also reported, along with the elastic (dotted line) and inelastic (dashed lines) contributions. The arrows indicate the approximate energy location of the excitations "bumps."

All the measured IXS spectra have been fitted using both one and two inelastic features, and the F test has been applied to the results in order to establish whether the second excitation is statistically necessary to describe the spectra: this is always the case for Q values larger than 4 nm^{-1}. The statistical significance of the two excitations fit of the spectrum at $Q = 4$ nm^{-1} is at the threshold. Previous IXS spectra at lower Q's (Ref. 6) have been reanalyzed and no evidence for the second peak has been found.

It is worth to note that, due to the weakness of the inelastic signal with respect to the intense elastic peak in this sample, the difference between the one- and two-excitation fits could not be appreciated from Fig. 1. However, beyond the quantitative statistical data analysis, the presence of two excitations clearly arise looking at the *longitudinal current* spectra, $C_L(Q,\omega) = (\omega^2/Q^2)S(Q,\omega)$, as it is evident in Fig. 2. As an example, in this figure we report for $Q = 6.5$ nm^{-1} the difference, multiplied by ω^2, between the IXS data and the $S_{el}(Q,\omega)$ determined by the fit (open circles with error bars). The broken lines represent $\omega^2 S_{inel}(Q,\omega)$ obtained by the previously described fit of the measured spectra with one (dash-dotted) or two (dashed) excitations. As can be easily seen, one single excitation does not account even qualitatively for the measured spectrum. Even if the agreement between the data and the two-excitations fit is not perfect, pointing out the need for a more complete generalized hydrodynamic model, it is clear that a two-excitation description of the spectra is compulsory in this Q region.

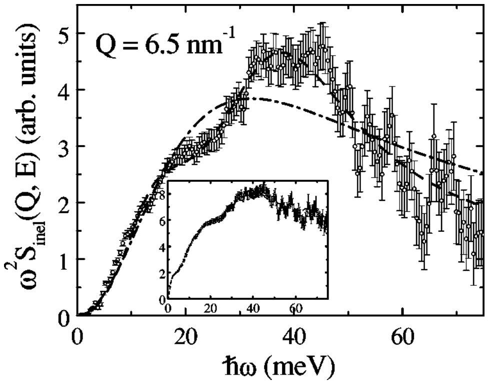

FIG. 2. The current spectrum of the inelastic part of the IXS signal (the elastic contribution to the fit is subtracted by the experimental data) at $Q = 6.5\ \mathrm{nm}^{-1}$ (open circles) is reported together with its $\pm\sigma$ error bars and the one- (dot-dashed) and two- (dashed) excitation fits. The inset shows the current spectra of the whole IXS signal, without subtraction of the elastic contribution, and the total fit to the spectrum (dashed line) including the elastic and inelastic (two-excitation) part.

To show that the need for a two-excitation representation of the data—as demonstrated in the main panel of Fig. 2—is not an artifact due to the subtraction of the elastic line, the ''experimental'' current spectra (raw IXS data multiplied by ω^2) is reported in the inset of Fig. 2. The presence of the (almost Lorentzian) resolution function manifests itself as a third bump at low energies (≈ 1.5 meV) and as a long (almost ω independent) tail. Besides these two resolution features, the presence of two excitations is evident also in the inset of Fig. 2, i.e., in the raw data.

The excitation energies obtained by the fit and the corresponding apparent sound velocities $[v(Q) = \Omega(Q)/Q]$ are reported in Figs. 3(a) and 3(b), respectively. Data from previous IXS measurements in vitreous silica,[5–7] performed at low Q are also reported. The corresponding dispersion curves obtained from numerical studies[13] as the maxima of the longitudinal and transverse currents are plotted in the same figure (open symbols). It is evident from Fig. 3 that the two excitations found by the fit analysis of the experimental data match with the LA and TA branches derived from the MD simulations. In particular, the lower-energy excitation in the IXS data is in very good agreement with the TA branch, and is then associated with the spilling of the TA excitation in the measured (longitudinal) spectra due to polarization mixing[14] that, in this glass, becomes effective for Q's larger than $\approx 5\ \mathrm{nm}^{-1}$.

The excitation at higher energy obtained from the fit of the measured spectra is associated to the LA mode: the $\Omega(Q)$ values obtained here are the extension at high Q's of the LA dispersion relation previously determined by IXS,[5–7] and are also in agreement with the trend of the LA branch derived from MD simulations. This branch shows a clear bend-up at $\approx 5\ \mathrm{nm}^{-1}$, i.e., the generalized sound velocity undergoes a speed-up from its low-Q value ($v \approx 6400$ m/s) to ≈ 9000 m/s.[19] The existence of a positive dispersion of the generalized sound velocity could be interpreted as the signature of an underlying relaxation process. This possibility, as well as the origin of this process—that cannot be identified with the structural (α) relaxation process, basically frozen in the glassy phase—is an open problem. In Ref. 15 it has been suggested that the origin of this relaxation process could be retrieved in the nature of the spatial pattern of the vibrational eigenmodes of a disordered structure, rather than in dynamical effects such as, for example, the anharmonicity of the vibrational dynamics. Further studies, specifically on the temperature dependence of this phenomena, are required to asses this point. It is important to mention that, by an INS study of the dynamics of v-silica (v-sitica) at large momentum transfer ($Q > 20\ \mathrm{nm}^{-1}$), Arai *et al.*[20] deduced a generalized sound velocity of ≈ 9400 m/s, a value compatible with the one found here in the high-frequency side of the transition. Finally, at Q larger than ≈ 7–$8\ \mathrm{nm}^{-1}$, the LA dispersion relation shows the features of the usual acoustic phonons behavior: it starts to bend down and reaches a maximum at half of the p-BZ edge ($\approx 11\ \mathrm{nm}^{-1}$ in vitreous silica).

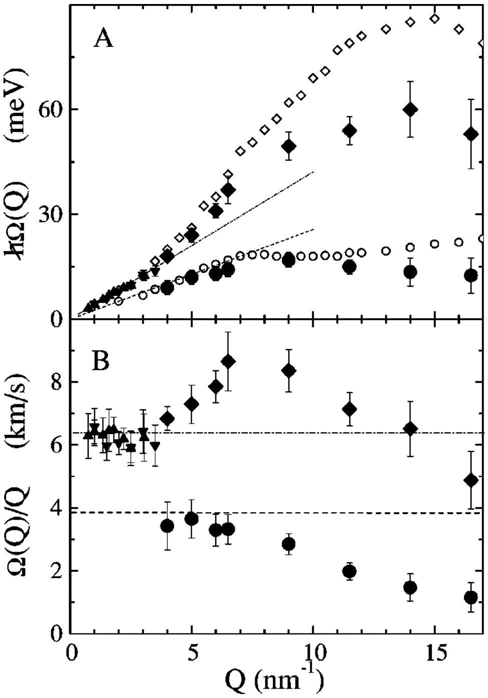

FIG. 3. (a) Dispersion relation of vitreous silica in the first p-BZ. Full symbols are experimental data (maxima of the two inelastic contributions to the current spectra) representing the excitation energies $[\hbar\Omega(Q)]$ of the longitudinal (diamond) and transverse (circle) branches. Data from $Q = 4\ \mathrm{nm}^{-1}$ are from present work, below $Q = 4\ \mathrm{nm}^{-1}$ are from Refs. 5–7 (triangles). The open symbols are the main maxima of the simulated L (open diamond) and T (open circle) current spectra from Ref. 13. Dash-dotted and dashed lines are the extrapolation of the low frequency L and T sound velocity, respectively. (b) Generalized sound velocity derived from the data of panel (a) as $v(Q) = \Omega(Q)/Q$. Symbols as in (a), the MD data are not reported.

In conclusion, in the present work we have studied the dynamics in the intermediate Q region (from 20% up to the first p-BZ edge) in vitreous silica. We have shown that, besides the usual propagating longitudinal sound modes already observed in glasses at ''small'' Q's (up to 20% of the p-BZ edge in v-silica), a second excitation becomes more and more evident in the spectra as Q is increased. This second excitation—in the Q range where it is visible—is almost non-Q dispersing and is assigned to the TA branch. The possibility to observe simultaneously the TA and LA excitations has allowed the detailed determination of the shape of the LA branch, which shows three distinct regions: (i) At Q below 4 nm^{-1} it linearly disperses with a sound velocity $v \approx 6400$ m/s, consistently with light-scattering measurements;[21] (ii) with increasing Q, it does not show tendency to saturation,[9] but, on the contrary, it reveals a speed-up, and it reaches a generalized sound velocity of ≈ 9000 m/s; (iii) at Q higher than 7 nm^{-1}, it starts to follow a crystallike behavior with a slow down and a maximum around half of the p-BZ. The observation in the LA branch of vitreous silica of a positive dispersion of the generalized sound velocity provides an important missing tile in the phenomenology of disordered induced features in glasses. As a speculation, a possible explanation for such a positive dispersion can be searched in the presence of a very fast ''relaxation'' process associated to the structural disorder, as suggested in Ref. 15, or in the interaction of the LA branch with other modes, a phenomenon similar to the symmetry avoided crossing in crystals.

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[19] It is worth to stress that while the actual values of $\Omega(Q)$ plotted in Fig. 3—and consequently those of $v(Q)$—can depend on the specific model used to represent the $S(Q,\omega)$, the existence of a positive dispersion of $v(Q)$ is a robust result. Indeed, in order to invalidate the existence of a positive dispersion of the $v(Q)$, the maximum of the spectrum at $Q = 6.5\ \mathrm{nm}^{-1}$ (which is found from the fit to be at $\Omega \approx 37$ meV) should sit at $\Omega \approx 27.5$ meV or less. Looking at the $Q = 6.5\ \mathrm{nm}^{-1}$ current spectrum reported in Fig. 2, one can easily recognize that this not compatible with the experimental data.

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