Communication: High-frequency acoustic excitations and boson peak in glasses: A study of their temperature dependence

B. Ruta,[1,a] G. Baldi,[1,2] V. M. Giordano,[1] L. Orsinger,[3] S. Rols,[4] F. Scarponi,[5] and G. Monaco[1]

[1]*European Synchrotron Radiation Facility, BP220, F-38043 Grenoble, France*
[2]*IPCF-CNR, UOS Roma, 00185 Roma, Italy*
[3]*Department of Physics, Trento University, 38050 Povo, Trento, Italy*
[4]*Institut Laue-Langevin, BP156, 38042 Grenoble, France*
[5]*Department of Physics, Perugia University, Via A. Pascoli, 06100 Perugia, Italy*

The results of a combined experimental study of the high-frequency acoustic dynamics and of the vibrational density of states (VDOS) as a function of temperature in a glass of sorbitol are reported here. The excess in the VDOS at ~4.5 meV over the Debye, elastic continuum prediction (boson peak) is found to be clearly related to anomalies observed in the acoustic dispersion curve in the mesoscopic wavenumber range of few nm^{-1}. The quasiharmonic temperature dependence of the acoustic dispersion curves offers a natural explanation for the observed scaling of the boson peak with the elastic medium properties. © *2010 American Institute of Physics*. [doi:10.1063/1.3460815]

The understanding of the vibrational properties of disordered systems remains an open problem in Condensed Matter Physics despite of the intense efforts dedicated to it in recent years.[1] The absence of a clear theoretical frame to serve as a reference and the difficulty of disentangling system specific effects from universal behaviors in both experimental and numerical simulation results makes in fact the progress in the field slow. In particular, an anomaly present in the vibrational density of states (VDOS), $g(E)$, at energies of few meV has attracted much interest due to its universal occurrence in glasses.[2] This anomaly is best evidenced as a broad bump, known as boson peak, appearing in the reduced density of states $g(E)/E^2$ over the Debye, elastic continuum prediction in an energy range where the Debye model still works reasonably well for the corresponding crystals. Its understanding then holds the promise to reveal information on the vibrational dynamics of glasses in the crucial energy range where it starts to behave distinctly different from the prediction of the Debye model.

Several theoretical models are able to justify a peak in the reduced density of states. In one class of models this peak is produced by the interaction of pure acoustic modes with quasilocal modes that would be present in real glasses as a consequence of the anharmonic nature of the interatomic potentials.[3] However, models built in terms of harmonic oscillators with disorder in the force constants are able as well to produce a similar peak.[4–6] Analogous results appear in models postulating spatially fluctuating elastic constants as a source of scattering for the sound waves.[7] Moreover, the boson peak has been recently interpreted as the signature of the breakdown of the classical elasticity description in glasses on the mesoscopic length scale of few nanometers.[8]

From an experimental point of view it is hard to distinguish between different models on the basis of a measurement of the boson peak alone. In order to make a step further, one approach has been to study in addition the acoustic excitations in the energy range of the boson peak and to compare their properties (velocity and attenuation) at a given temperature in the glass to the predictions of the different available models in order to perform a more stringent test.[7,9] Both sound velocity and attenuation show, in fact, specific signatures in the boson peak energy range.[10,11] Another approach has been to compare the dependence of the boson peak on a control parameter, such as pressure[12–14] or temperature,[15,16] to the corresponding dependence of the sound velocities in order to investigate the connection between boson peak and elastic properties. For the time being, the available results are still scarce and do not lead to a clear picture: In some cases the boson peak follows the corresponding transformation of the elastic medium,[12,17] but not in all cases.[13,14] The role played by anharmonic effects on the elastic properties has been proposed to be very relevant for a correct understanding of these comparisons.[16]

In this communication a step further in this study is made by performing a detailed investigation of the vibrational properties of a glass of sorbitol combining both of the approaches above, i.e., comparing the temperature dependence of the boson peak to that of the elastic properties measured at low frequency and studying the temperature dependence of the acoustic excitations at energies comparable to the boson peak position. In particular, the boson peak has been measured as a function of temperature using inelastic neutron scattering (INS), and it is shown to follow the corresponding transformation of the elastic medium. The longitudinal acoustic dispersion curves in the meV energy range have been measured as a function of temperature using inelastic x-ray scattering (IXS). Their temperature dependence follows closely that of the macroscopic sound velocity, and this is true, in particular, in the energy range of the boson peak, where specific anomalies appear. A quasiharmonic

a)Electronic mail: ruta@esrf.fr.

mechanism rules the temperature variation of the sound velocity, and it is proposed to be at the origin of the observed scaling of the boson peak with the elastic continuum properties. This observation strongly suggests a close connection between boson peak and elastic properties on the mesoscopic length-scale of few nanometers.

IXS measurements of glassy sorbitol were performed at the beamline ID16 of the ESRF, using an incident beam of 23.724 keV and with an instrumental resolution of 1.3 meV full width at half maximum (FWHM). Dynamic structure factor spectra $S(q, E)$ have been collected in the exchanged momentum q range between 1.3 and 11 nm^{-1} at several temperatures in the glassy phase. A cylindrical sample 17 mm in length along the incident beam direction was employed. In addition, INS measurements of the VDOS were performed at the time-of-flight spectrometer IN4 of the ILL, using an incident wavelength of 2.7 Å and an energy resolution of 0.6 meV FWHM. In this case a disk-shaped sample 200 μm thick and with a diameter of 5 cm was used, corresponding to a 91% transmission at the used wavelength. In all cases, the glasses of sorbitol ($C_6H_{14}O_6$, glass transition temperature $T_g = 266$ K, and melting temperature $T_m = 368$ K)[18] have been prepared using 99% purity powder purchased from Sigma-Aldrich (France), melted and kept for some hours under vacuum at ~380 K, and then quenched in liquid nitrogen. It is worth mentioning that sorbitol is a molecular glass with a high fragility index of ~ 100,[19] despite showing elastic properties similar to those of glass-formers with lower fragility, such as high shear and longitudinal modulus.[20,21] These features, together with a quite high boson peak position (~4.5 meV), make of sorbitol a very good candidate for a detailed investigation of the acoustic properties in the boson peak region using IXS since they partly counterweight the difficulties deriving from the limited energy resolution of the technique.

The INS data have been treated with the standard time-of-flight to energy conversion and have been corrected for the aluminum empty cell signal and an angle-independent multiple scattering contribution.[22] Special attention has been used to set these data on an absolute scale, in order to allow for a direct comparison to the expected low-energy Debye limit $g_D(E)/E^2 = 3/E_D^3$, where E_D is the Debye energy.[23] The temperature dependence of the reduced VDOS is reported in the upper panel of Fig. 1. On decreasing the temperature in the glassy phase, the intensity of the boson peak decreases as well. The observed temperature dependence can be accounted for by the transformation of the elastic medium. Indeed, by replotting the reduced VDOS in Debye units, all curves rescale on a single one in the peak region (lower panel of Fig. 1), similar to what observed in Refs. 12 and 17. Although small differences remain in the low energy range of the spectra, the overall validity of the scaling procedure suggests a strong relation between boson peak and elastic properties.

In order to investigate in more detail this relation, the high-frequency acoustic dynamics of glassy sorbitol has been probed using IXS. Examples of the spectra collected at the lowest investigated temperature (80 K) are reported in Fig. 2 for three different exchanged momentum (q) values. The
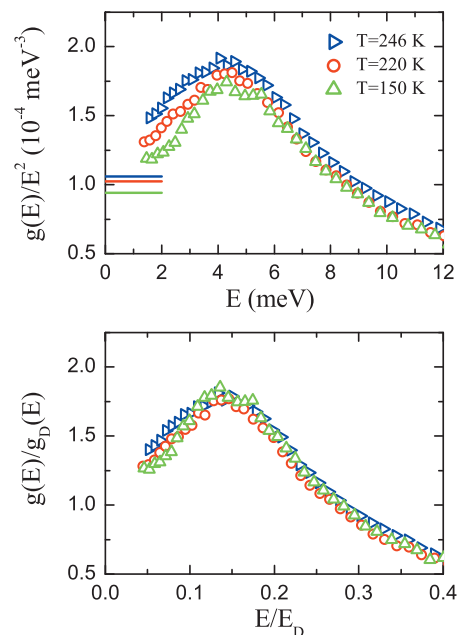

FIG. 1. Upper panel: reduced VDOS of glassy sorbitol for different temperatures, together with the indication of the corresponding Debye level (horizontal lines). Lower panel: same data as above after rescaling in Debye units.

spectra obtained in this experiment have been analyzed using as fitting function the convolution of the instrumental resolution with an expression describing the elastic line with a Dirac delta function and the inelastic signal with a damped harmonic oscillator (DHO) model.[10] In Fig. 2 the experimental data are reported together with the best fitting functions, the corresponding inelastic components of the spectra (Brillouin peaks, corresponding to longitudinal acoustic excitations), and the instrumental resolutions utilized in the convo-
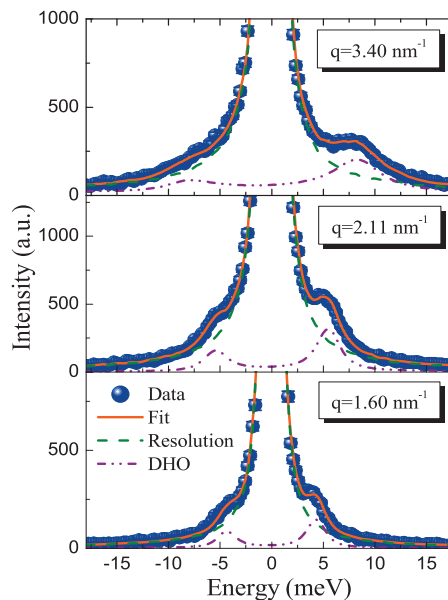

FIG. 2. Brillouin spectra of a sorbitol glass measured at 80 K and at the indicated q-values. For all spectra the best fitting line shapes based on the DHO model are reported as well (red full lines), together with the corresponding inelastic components (violet dotted-dashed lines) and the instrumental functions (green dashed lines).
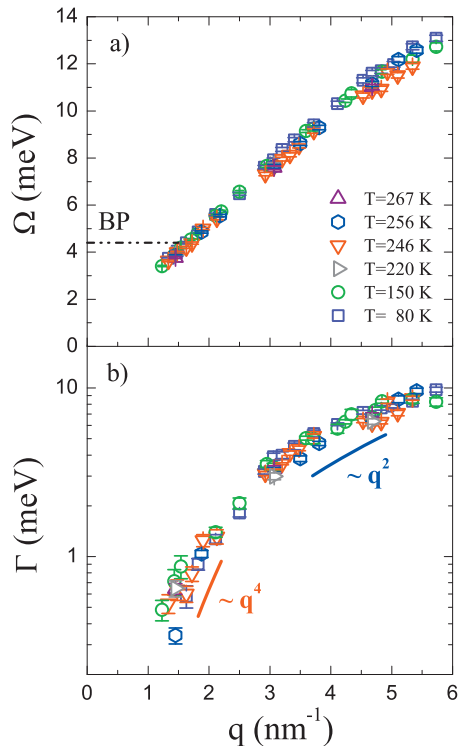
FIG. 3. Inelastic x-ray scattering results for the q-dependence of the energy position (a) Ω and broadening (b) Γ of the longitudinal acoustic excitations of glassy sorbitol at the indicated temperatures. In (a) the horizontal line marks the boson peak position. In (b) the two lines emphasize the change in the q-dependence of Γ from a power law compatible with q^4 at low q to one compatible with q^2 at high q.

FIG. 4. (a) Inelastic x-ray scattering results for the apparent sound velocity $v_l=\Omega/(q\hbar)$ of the longitudinal acoustic excitations of glassy sorbitol at the indicated temperatures. The macroscopic limits for the sound velocity obtained from BLS measurements (Ref. 21) are reported as well (horizontal lines). The vertical dotted-dashed line marks the q-value corresponding to the boson peak position via the dispersion relation of Fig. 3. (b) Same data as in (a) but rescaled for the macroscopic sound velocity.

lution procedure. The energy position Ω and broadening (FWHM) Γ of the longitudinal acoustic excitations derived in this way for the different investigated q's and temperatures are reported in Fig. 3. In particular, in Fig. 3(a) the acoustic dispersion curve, $\Omega(q)$, is reported for the various probed temperatures, and shows a seemingly linear region at low q. In Fig. 3(b) the q-dependence of Γ is instead reported in log-linear scale for the different considered temperatures. This parameter is strongly q-dependent, changing continuously from $\sim q^4$ at low-q to $\sim q^2$ at high-q, thus supporting the universality of the low-q q^4 dependence previously observed in other few glasses.[10,24,25] In particular, it was here possible to obtain reliable measurements of Γ down to ~ 1.3 nm^{-1}, where Γ is only about one-fourth of the FWHM of the instrumental function. The interesting new information here is the temperature independence of Γ, which extends similar observations previously limited to the high-q q^2-range,[26] and confirms the nondynamic origin of Γ in the whole explored q-range. In Fig. 4(a) the longitudinal apparent phase velocity $v_l=\Omega/(q\hbar)$ is reported as a function of q for the different temperatures. The data do not show the smooth, sinelike decrease proposed from earlier experimental results.[27] Rather, they present an abrupt decrease from the macroscopic value (horizontal line, from Ref. 21) to a lower plateau at ~ 2 nm^{-1}, while only for higher q values they show the expected sinelike decrease on approaching the border of the pseudo-Brillouin zone (half of the first sharp diffraction peak position). Using Fig. 3(a) to convert energies into q values, it is easy to realize that this flattening of the
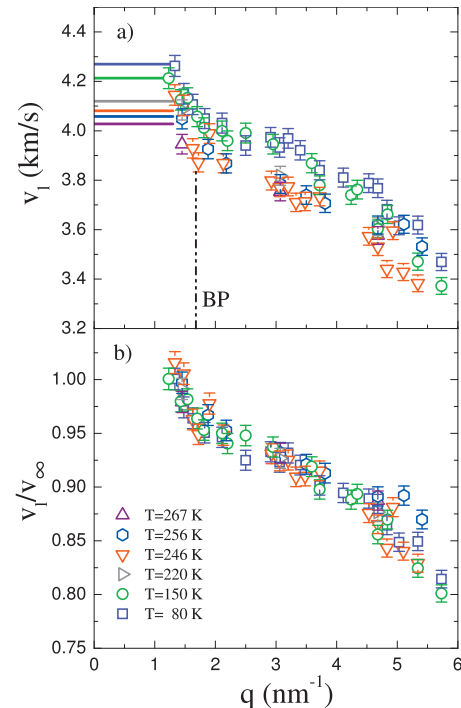
sound velocity appears exactly in the energy range of the boson peak and, of course, a flattening of the sound velocity implies an excess of acoustic modes in the VDOS over the Debye, continuum medium prediction. This result confirms those recently found in glassy glycerol:[10] the Debye continuum approximation in glasses holds up to ~ 1 nm^{-1} and above that it undergoes an abrupt breakdown, while it still works reasonably well in the same q range for the corresponding crystals. It is worth emphasizing that this anomalous behavior of the high-frequency sound velocity appears in the same q range where the peculiar q^4 dependence of the broadening Γ is detected, clearly indicating that these two features must be strictly related. Moreover, as for the case of glassy glycerol,[10] it is possible to quantitatively reproduce the boson peak starting from the measured dispersion and broadening of the high frequency acoustic excitations.

Differently from the case of glycerol,[10] in sorbitol the IXS apparent sound velocity reaches the macroscopic one already at the lowest probed q-values, thus indicating the absence of relevant anharmonic, relaxational, and/or other q-dependent effects in the frequency interval comprised between the terahertz range probed by IXS and the 10 GHz range probed by Brillouin light scattering (BLS). The BLS sound velocity data show a linear temperature dependence[21] which can be ascribed to a simple quasiharmonic mechanism, i.e., to the change of density with temperature.[28,29] Here it is interesting to observe that the temperature dependence of the IXS apparent sound velocity curve follows that of the macroscopic one in the whole explored q-range and, in

particular, in the region where the plateau at ~ 2 nm^{-1} in the apparent sound velocity is observed: The shape of the dispersion curves in this interesting range then turns out to be temperature independent. This observation is verified in Fig. 4(b), where the IXS sound velocity data at the different temperatures are reported after rescaling for their macroscopic limit. A single curve is obtained: The dispersion curves in the explored q range follow the modifications of the elastic medium. Thus a very similar phenomenology to the one emerging from Fig. 1 appears here: The temperature dependence of the elastic properties dictates that of both the boson peak and of the acoustic excitations in the corresponding energy range, thus making even stronger the connection between acoustic excitations in the mesoscopic range and the boson peak in glasses.

In conclusion, the temperature dependence of the high-frequency acoustic dispersion curves of glassy sorbitol can be described to a good approximation within a quasiharmonic approach, while the corresponding acoustic damping (Γ) is definitively nondynamic in origin. Peculiar anomalies are found both in the acoustic dispersion and damping which appear in the same energy range of the boson peak, thus suggesting a strong connection between acoustic properties in the mesoscopic range and boson peak. Moreover, the study of the temperature dependence of these properties shows that this connection is kept under temperature changes. These results then lead to a natural frame for justifying and understanding the observed scaling of the boson peak with the parameters of the elastic medium. Glasses with anharmonic and/or relaxational contributions larger than in sorbitol and for which the quasiharmonic approximation does not hold might however show a more complex phenomenology.

[1] See, for example, 10th International Workshop on Disordered Systems, edited by A. Fontana, P. Verrocchio, and G. Viliani, Philos. Mag. **87** (2007).

[2] V. K. Malinovsky, V. N. Novikov, and A. P. Sokolov, Phys. Lett. A **153**, 63 (1991).

[3] V. L. Gurevich, D. A. Parshin, and H. R. Schober, Phys. Rev. B **67**, 094203 (2003).

[4] W. Schirmacher, G. Diezemann, and C. Ganter, Phys. Rev. Lett. **81**, 136 (1998).

[5] S. N. Taraskin, Y. L. Loh, G. Natarajan, and S. R. Elliot, Phys. Rev. Lett. **86**, 1255 (2001).

[6] T. S. Grigera, V. Martín-Mayor, G. Parisi, and P. Verrocchio, Nature (London) **422**, 289 (2003).

[7] W. Schirmacher, G. Ruocco, and T. Scopigno, Phys. Rev. Lett. **98**, 025501 (2007).

[8] F. Léonforte, A. Tanguy, J. P. Wittmer, and J.-L. Barrat, Phys. Rev. Lett. **97**, 055501 (2006).

[9] B. Rufflé, D. A. Parshin, E. Courtens, and R. Vacher, Phys. Rev. Lett. **100**, 015501 (2008).

[10] G. Monaco and V. Giordano, Proc. Natl. Acad. Sci. U.S.A. **106**, 3659 (2009).

[11] G. Monaco and S. Mossa, Proc. Natl. Acad. Sci. U.S.A. **106**, 16907 (2009).

[12] A. Monaco, A. I. Chumakov, G. Monaco, W. A. Crichton, A. Meyer, L. Comez, D. Fioretto, J. Korecki, and R. Rüffer, Phys. Rev. Lett. **97**, 135501 (2006).

[13] K. Niss, B. Begen, B. Frick, J. Olliver, A. Beraud, A. Sokolov, V. N. Novikov, and C. Alba-Simionesco, Phys. Rev. Lett. **99**, 055502 (2007).

[14] L. Hong, B. Begen, A. Kisliuk, C. Alba-Simionesco, V. N. Novikov, and A. P. Sokolov, Phys. Rev. B **78**, 134201 (2008).

[15] S. Caponi, A. Fontana, F. Rossi, G. Baldi, and E. Fabiani, Phys. Rev. B **76**, 092201 (2007).

[16] G. Baldi, A. Fontana, G. Monaco, L. Orsingher, S. Rols, F. Rossi, and B. Ruta, Phys. Rev. Lett. **102**, 195502 (2009).

[17] H. Shintani and H. Tanaka, Nature Mater. **7**, 870 (2008).

[18] R. A. Talja and Y. H. Roos, Thermochim. Acta **380**, 109 (2001).

[19] L.-M. Wang, C. A. Angell, and R. Richert, J. Phys. Chem. **125**, 074505 (2006).

[20] K. Niss, C. Dalle-Ferrier, V. M. Giordano, G. Monaco, B. Frick, and C. Alba-Simionesco, J. Chem. Phys. **129**, 194513 (2008).

[21] B. Ruta, G. Monaco, F. Scarponi, and D. Fioretto, Philos. Mag. B **88**, 3939 (2008).

[22] E. Fabiani, A. Fontana, and U. Buchenau, J. Chem. Phys. **128**, 244507 (2008).

[23] We recall that $E_D = k_D v_D$, with $k_D = (6\pi^2 \rho/M)^{1/3}$ and $v_D = [(1/3)(v_l^{-3} + 2v_t^{-3})]^{-1/3}$, where ρ is the mass density, M is the molecular mass, and v_t (v_l) is the transverse (longitudinal) sound velocity. Here v_l is taken from Ref. 21, and v_t from unpublished Brillouin scattering data.

[24] B. Rufflé, M. Foret, E. Courtens, R. Vacher, and G. Monaco, Phys. Rev. Lett. **90**, 095502 (2003).

[25] B. Rufflé, G. Guimbretière, E. Courtens, R. Vacher, and G. Monaco, Phys. Rev. Lett. **96**, 045502 (2006).

[26] G. Ruocco, F. Sette, R. Di Leonardo, D. Fioretto, M. Krisch, M. Lorenzen, C. Masciovecchio, G. Monaco, F. Pignon, and T. Scopigno, Phys. Rev. Lett. **83**, 5583 (1999).

[27] F. Sette, M. H. Krisch, C. Masciovecchio, G. Ruocco, and G. Monaco, Science **280**, 1550 (1998).

[28] F. Birch, J. Geophys. Res. **65**, 1083 (1960).

[29] F. Birch, J. Geophys. Res. **66**, 2199 (1961).