Connection between Boson Peak and Elastic Properties in Silicate Glasses

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Inelastic neutron, light, and x-ray scattering are used to investigate the vibrational density of states (VDOS) and the elastic properties of a sodium silicate glass as a function of temperature. The elastic moduli show the frequency and temperature dependence typical of anharmonic effects. The measured VDOS spectra, up to and including the excess vibrational density at the boson peak, scale with the Debye level only if this is calculated from the high-frequency values of the elastic constants. This emphasizes that conclusions on the relation between VDOS and elastic properties can be drawn only if anharmonic and relaxational effects are properly taken into account.

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A common feature in the density of vibrational states, $g(E)$, of glasses and supercooled liquids is the presence of an excess of modes over the Debye level known as boson peak (BP). It appears in Raman and neutron scattering (NS) spectra as a peak in $g(E)/E^2$ for $E \sim 2$–6 meV. In specific heat, C_P, measurements it corresponds to a peak in C_P/T^3 at temperatures around 10 K [1]. Despite the long-standing interest in this glass-specific excess of modes, its origin still remains poorly understood.

Many different theoretical approaches have been followed to describe the low-energy vibrations in glasses. In one approach, for example, a "soft" anharmonic nature for the potentials is assumed, leading to "quasilocal" modes coexisting and hybridizing with the sound waves at the BP [2,3]. This class of models has the strength of being an extension of the phenomenological description of the thermal properties of glasses at temperatures below 1 K in terms of two level systems [4]. In another class of approaches, the atoms are assumed to vibrate harmonically in the arrested glass configuration characterized in terms of randomly fluctuating elastic constants [5–7]. In a third class of approaches, the vibrations of the glass are studied looking at the properties of the complex energy landscape, and the BP has been attributed to the transition between a minimum-dominated and a saddle-dominated phase [8], or to the onset of strongly anharmonic transitions between local minima [9].

On the experimental side, it is useful to emphasize that below the BP energy position a quasielastic scattering (QES) contribution is usually observed in the Raman [10] and NS [11] spectra. In silica, for example, the origin of this QES has been explained in terms of relaxational and anharmonic effects [12,13]. This broadening of the elastic line covers the low-energy side of the BP so that the Debye level is never clearly attained in the experimentally measured VDOS. The comparison with the macroscopic, Debye level resides instead on independent measurements of density and sound velocities, the latter ones being usually obtained by means of ultrasonic or Brillouin light scattering techniques in the MHz or GHz frequency range, respectively. This need of combining different experimental techniques leads to the fact that going from the simple qualitative observation of the existence of the BP to a quantitative understanding of its connection to the macroscopic properties is a complex task that has been accomplished in detail in only a few glasses. In particular, the BP has been measured as a function of macroscopic parameters like temperature in silica [13,14], pressure in few polymers [15,16], and density in both a silicate glass [17] and in GeO_2 [18], and varying the sample preparation in a silicate glass [19] and in an epoxy-amine mixture during chemical vitrification [20].

The existing studies agree on the following points. (i) The BP shifts towards higher energies and appears with weaker intensity on increasing the sample density. (ii) The shape of the BP is invariant: spectra corresponding to different densities collapse on a single master curve if plotted as a function of E/E_{BP}, E_{BP} being the BP maximum. However, controversial results have been reported on the density dependence of E_{BP}. In particular, a nuclear inelastic scattering study [17] has shown that in permanently densified silicate glasses the BP shift follows the variation of the Debye energy E_D as far as no local structure modifications take place. A similar result has been recently reported using numerical simulations of systems with a varying degree of fragility [21]. On the contrary, a pressure dependence for E_{BP} stronger than for E_D has been reported in studies of polymeric glasses [15,16]. These controversial results need to be better understood, since they question whether it is possible or not to establish a direct relation between the low-energy excess of modes and the elasticity in glasses. This point is clearly central in order to discriminate between the different existing theoretical models.

With the aim of shedding some light on this issue, we report in this Letter on a detailed experimental investigation of the vibrational dynamics of a sodium silicate glass. We show in what follows that in this system the sound velocities have a non-negligible frequency dependence, and that only carefully taking their values in the purely elastic limit the scaling of $E_{\rm BP}$ with E_D is recovered. This implies that a thorough knowledge of the vibrational dynamics of a glass is mandatory before any conclusion on the relation between the BP and the properties of the continuum medium can be drawn.

The glass chosen for this study is 60%SiO_2-40%Na_2O. The inclusion of Na in the SiO_2 network induces a strong reduction of the glass transition temperature ($T_g \sim 700$ K) [22] and an increase of the fragility parameter ($m \sim 50$) [23] with respect to pure v-SiO_2. The samples have been prepared by melting pure SiO_2 and Na_2CO_3 at 1600 °C in air in a Pt crucible and then annealing the obtained glass for 6 h at the glass transition temperature. The produced sample is a disk 5 cm in diameter and 3.5 mm in height, corresponding to a 9% scatterer at the wavelength used for the NS experiment. Moreover, a small portion of the same sample has been used for Brillouin light scattering (BLS) and inelastic x-ray scattering (IXS) measurements in the GHz and THz frequency range, respectively.

The NS experiment was carried out at the thermal neutron spectrometer IN4 at the ILL in Grenoble. The chosen neutron wavelength of 2.2 Å provides an energy resolution of 0.8 meV FWHM (elastic line) and gives access to the wave vector range $0.8 < q < 5.4$ Å^{-1} at the BP energy. The NS data have been treated using standard conversion of time of flight into energy and corrected for the aluminum empty cell signal. An angle-independent multiple scattering contribution has been subtracted from the data, following the procedure described in Ref. [24]. The resulting spectra are essentially proportional to the dynamic structure factor, $S(q, E)$, since the total incoherent cross section of the studied system is 14% of the coherent one. A lower neutron wavelength of 0.74 Å, giving access to a wider q range, was used to measure the static structure factor $S(q)$, to which the obtained spectra have been normalized. The corrected spectra, averaged over the spanned wave vector range, are reported in Fig. 1 as a function of energy at the six measured temperatures between 100 and 600 K. They show a BP-like feature located at about 6 meV and a QES contribution below 2.5 meV. The QES intensity increases with temperature and is most clearly visible at 600 K over the tail of the instrumental resolution determined from a measurement on a vanadium scatterer.

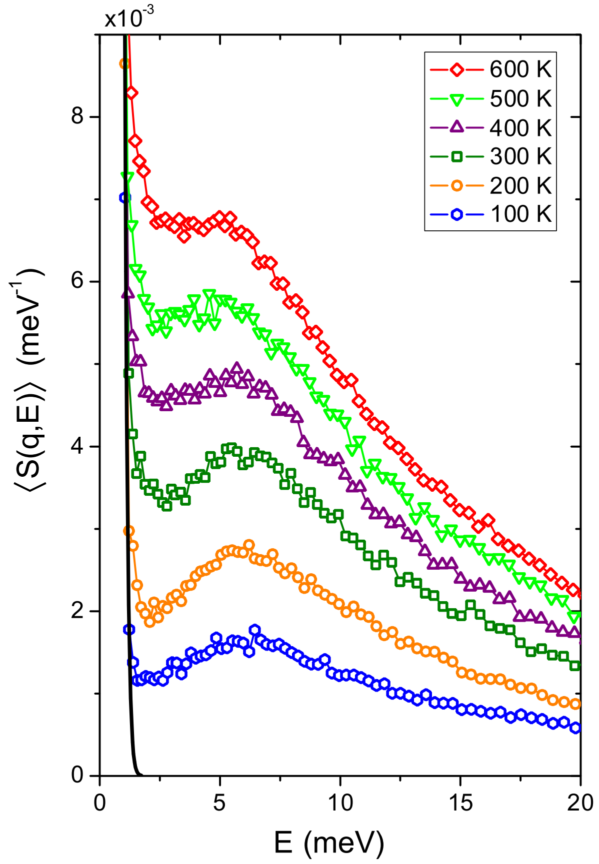

FIG. 1 (color online). Dynamic structure factor spectra of a 60%SiO_2-40%Na_2O glass averaged over the $0.8 < q < 5.4$ Å^{-1} q range. The spectra are reported on an absolute scale and are measured at the indicated temperatures. The continuous line is a Gaussian fit to the instrumental resolution function and is normalized to the elastic peak of the 600 K spectrum. The quasielastic contribution below 2.5 meV is negligible at 100 K and broadens on increasing the temperature.

Based on the results reported for silica [12,13], the presence of a QES contribution suggests that thermally activated relaxations and anharmonicity affect the propagation of the sound waves. In order to clarify this point, and to study the connection between the vibrational density of states and the properties of the continuum medium, the acoustic properties need to be studied. In particular, the temperature dependence of the longitudinal v_L and transverse v_T sound velocity has been measured using a BLS setup in right-angle geometry with an incident wavelength of 5145 Å. The scattered light was analyzed using a Sopra DPDM monochromator [25] operating in single pass configuration at the 11th order, providing a resolution of 1.2 GHz. The longitudinal sound velocity data around room temperature have been confirmed using a Fabry-Perot spectrometer in backscattering geometry with an accuracy higher than 0.1%. The refractive index value $n = 1.52$, determined with the prism coupling technique on the same sample, was used to compute the sound velocities from the Brillouin peaks positions. The sound velocity values obtained in the BLS frequency region (10–30 GHz) show for both polarizations a marked decrease as temperature is increased, as shown in Fig. 2. This is

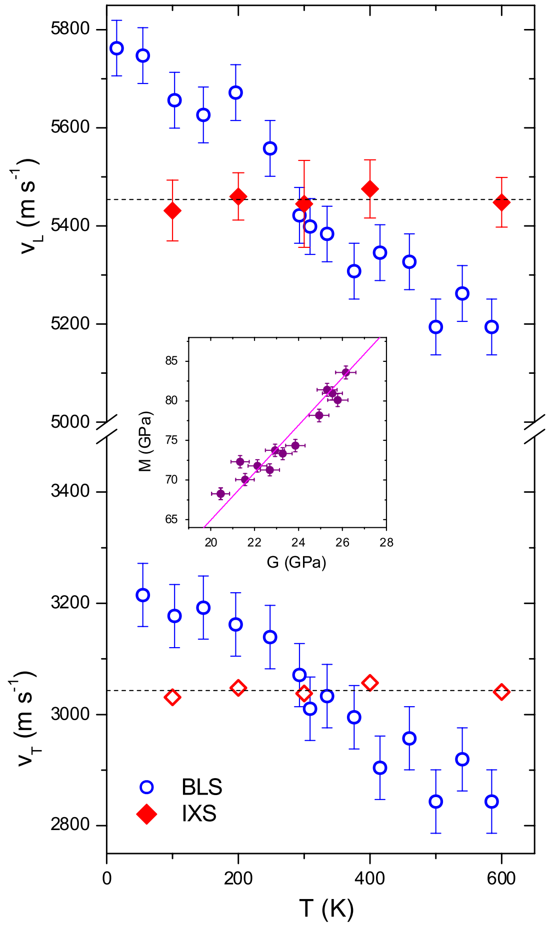

FIG. 2 (color online). Temperature dependence of the longitudinal, v_L, and transverse, v_T, sound velocity of a 60%SiO_2-40%Na_2O glass. Open circles: BLS data, full diamonds: IXS data. The high-frequency transverse sound velocity (open diamonds) is determined from the Cauchy-like relation as explained in the text. The dashed lines correspond to the best-fitted longitudinal and transverse sound velocities in the high-frequency limit. Inset: longitudinal modulus versus shear modulus from the BLS data. The line is a linear fit, with slope $B = 3$.

indeed very typical of anharmonic effects active in the probed frequency range [26].

The appearance of anharmonic effects in the BLS data implies that the measured sound velocities are frequency dependent and do not correspond to the infinite-frequency limit needed to characterize the elastic properties of the continuum medium. In order to obtain the appropriate sound velocity values, it is necessary to probe the acoustic dynamics at even higher frequencies. For this reason, an IXS experiment has been performed at the beam line ID16 of the ESRF, using a setup providing an energy resolution of 1.4 meV. The longitudinal sound velocity has been measured at few temperatures between 100 and 600 K and at a small exchanged wave vector, $q = 0.12$ Å^{-1}. The IXS results are compared to the BLS ones in the upper part of Fig. 2. The IXS sound velocities do not show any appreciable temperature dependence within the error bars, thus confirming that anharmonic effects are modifying the propagation properties of the acoustic waves in the GHz frequency range probed by BLS. It is worth noting that the low-temperature BLS data are higher than the IXS ones. This is in agreement with recent IXS results on glassy glycerol, where a characteristic negative dispersion of the sound velocity—strictly connected with the excess of states at the BP—has been reported for acoustic energies around E_{BP} [27]. The silicate glass studied here seems to show a similar phenomenology.

The IXS sound velocity data can be used to obtain the longitudinal sound velocity in the high-frequency, purely elastic limit. The corresponding values for the transverse sound velocity are more difficult to obtain since they are not directly accessible by IXS. They can, however, be estimated using the Cauchy-like equation $M = A + BG$: in fact, this linear relation between the longitudinal modulus, $M = \rho v_L^2$, with ρ the mass density, and the shear modulus, $G = \rho v_T^2$, has been shown to hold at every frequency [28], with a slope $B \sim 3$ and a system dependent constant A. This relation is confirmed by our BLS data, as shown in the inset of Fig. 2, and allows estimating the high-frequency transverse sound velocities corresponding to the measured longitudinal ones. The obtained values are plotted as open diamonds in the lower part of the figure. Finally, the dashed lines in the same figure are the best-fitted IXS sound velocities and are used to calculate the temperature dependence of the Debye energy in the purely elastic limit:

$$E_D(T) = \hbar q_D v_D(T). \tag{1}$$

Here $q_D = (6\pi^2\rho/\bar{m})^{1/3}$, with $\bar{m}$ the average atomic mass, and v_D is the Debye velocity.

The density of vibrational states has been computed from the NS spectra using the incoherent approximation and following the iterative procedure described in Ref. [24]. A first guess to the VDOS is obtained by fitting $S(q, E)$ using a q^2 wave vector dependence. The method then proceeds iteratively by computing the intermediate scattering function in the incoherent approximation, from which a refined VDOS is obtained by Fourier transforming back to the frequency domain. The convergence is usually reached after a few iterations. This approach allows obtaining both the VDOS and the wave vector dependence of the Debye-Waller factor taking into account the multiphonon contributions.

The temperature dependence of the VDOS divided by the Debye density of states $g_D(E) = 3E^2/E_D^3$ is plotted in Fig. 3 as a function of energy in Debye units. In the upper panel the high-frequency, IXS value of the Debye energy, E_D^{IXS}, is used. The lower panel shows the same scaling performed, however, using the BLS sound velocity values to calculate the Debye energy, E_D^{BLS}.

This figure clearly shows that the BP scales with the Debye level if the high-frequency, IXS values of the sound velocity are used. These are the correct values for the

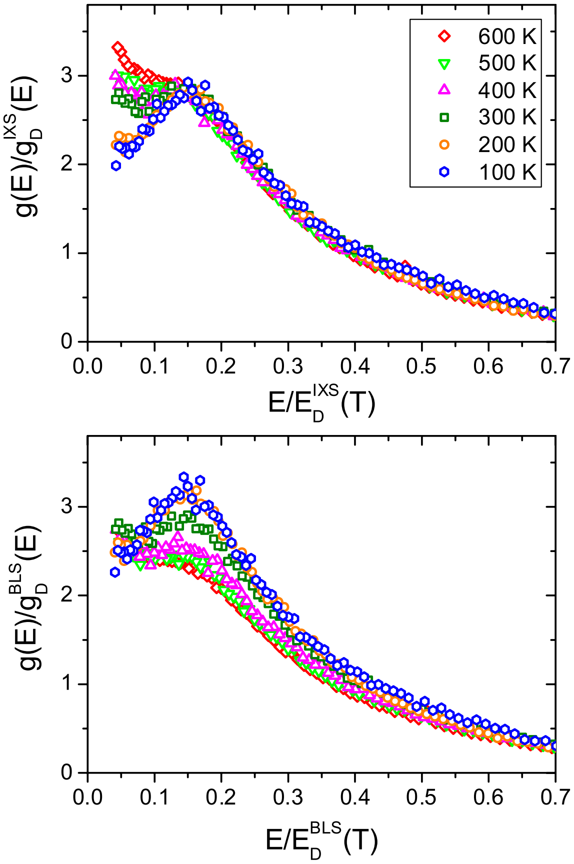

FIG. 3 (color online). Upper panel: VDOS in Debye units, where the Debye energy is determined starting from the high-frequency IXS values of the sound velocities. Lower panel: VDOS in Debye units, but with Debye energy values calculated starting from the BLS data, and thus affected by anharmonic effects.

sound velocity to be considered, since the Debye approximation rests on the idea of an elastic continuum. It is, moreover, interesting to directly observe in the lower panel of Fig. 3 that the determination of the Debye energy starting from the BLS data introduces a spurious shift of the BP both in energy and in intensity.

In conclusion, we confirm here that the VDOS spectra measured as a function of temperature over an energy range including the BP scale on a single master curve when plotted in Debye units [17,19]. Therefore, the present result gives further support to the strong connection between the glass-specific excess of modes giving rise to the BP and the elastic properties of the medium [17,19–21]. The existing theoretical approaches will have to incorporate this experimental result. At the same time, we underline the danger of drawing conclusions on this connection when the elastic properties of the glass have not been thoroughly characterized: the existence of overlooked relaxation or anharmonic effects might lead to wrong conclusions. In particular, it will be interesting to check whether the polymeric systems studied in this connection so far [15,16] are real counterexamples of the relation between BP and elastic properties, or whether the existence of anharmonic or secondary relaxations effects—likely present in these systems—might change the picture.

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