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Influence of Pressure on the Boson Peak: Stronger than Elastic Medium Transformation

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We study the changes in the low-frequency vibrational dynamics of poly(isobutylene) under pressure up to 1.4 GPa, corresponding to a density change of 20%. Combining inelastic neutron, x-ray, and Brillouin light scattering, we analyze the variations in the boson peak, transverse and longitudinal sound velocities, and the Debye level under pressure. We find that the boson peak variation under pressure cannot be explained by the elastic continuum transformation only. Surprisingly, the shape of the boson peak remains unchanged even at such high compression.

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A major peculiarity of the vibrational spectra of disordered materials is the existence of characteristic low-frequency vibrations, the so-called boson peak (BP). They appear, e.g., in Raman and neutron scattering spectra at energies $\sim 2\text{--}5$ meV or in specific heat measurements at $T \sim 3\text{--}10$ K and are ascribed to an excess vibrational density of states relative to the Debye level, which describes an elastic continuum. Although the BP is observed for almost all disordered systems, the microscopic nature of these excess vibrations and their possible connection to the glass transition or glass structure [1,2] remain the subject of active discussion. The BP appears in the energy range where the acoustic phonons have a wavelength of the order of a few nanometers, a typical length scale involved in glass transition theories [3,4]. There is a growing theoretical interest in a possible connection between the boson peak and a length scale at which the continuum elastic description breaks down [2].

The boson peak has been studied mainly as a function of temperature, sometimes as a function of thermal history, but rarely as a function of pressure. Moreover, the existing studies are often performed by Raman scattering [5–9] in which the shape, position, and intensity of the boson peak are altered by the light to vibration coupling factor. The latter by itself is pressure-dependent [10]. Relevant pressure studies of the boson peak by other techniques include low temperature heat capacity of polystyrene [11], neutron scattering studies on polybutadiene [12] or on permanently densified vitreous SiO_2 [13,14], and nuclear inelastic scattering (NIS) on densified $\text{Na}_2\text{FeSi}_3\text{O}_3$ [15]. A decrease of the boson peak intensity and an increase of the boson peak energy E_{BP} have been reported in all of these studies. Microscopic understanding of the underlying phenomena requires, however, the analysis of a broad number of other parameters that change under compression.

This Letter presents a detailed study of inelastic neutron (INS), Brillouin light (BLS), and inelastic x-ray (IXS) scattering spectra of poly(isobutylene) (PIB) at pressures

up to 1.4 GPa that corresponds to a significant change of density $\approx 20\%$. This unique combination of data allows direct comparison of pressure-induced variations of sound waves (even those in the energy range of the boson peak) with the variations of the boson peak. The analysis demonstrates that the boson peak variations cannot be described by a simple elastic continuum deformation alone: its frequency increases more strongly than the sound velocity, while the amplitude relative to the Debye level might slightly increase. Surprisingly, the spectral shape of the peak remains unchanged.

PIB polymer ($M_w = 3580$ g/mol, $M_n = 3290$ g/mol, $T_g \sim 195$ K, from Polymer Standard Service) has been used in all three experiments. All of the measurements were performed deep in the glassy state at $T = 140$ K, where the quasielastic contribution is not significant [16]. Pressure changes were made at high T (at 430 K for INS, at room T otherwise) followed by isobaric cooling down to 140 K. The INS experiment was performed at the time-of-flight spectrometer IN5 at the Institut Laue-Langevin (ILL) using $\lambda = 5$ Å, which gives an energy resolution of $\text{FWHM} = 103$ μeV . The pressure was applied using a clamp pressure cell allowing a change of pressure *in situ*. The sample transmission of PIB (94% incoherent scattering) was 88%. The IXS experiment was performed on the European Synchrotron Radiation Facility (ESRF) beam line ID28 with an energy resolution of $\text{FWHM} = 1.6$ meV, in a Q range from 2 up to 6 nm^{-1} . A piston-and-cylinder device was used with ethanol as the pressurizing medium, isolated from the sample by a Teflon film. Spectra were measured at atmospheric pressure and at $P = 0.3$ GPa. BLS spectra were measured in symmetric scattering geometry in an anvil cell using a tandem Fabry-Perot interferometer. The advantage of the symmetric scattering geometry is a compensation of the refractive index [17] that excludes influence of its pressure variations on the obtained results. To estimate the influence of thermodynamic path on the BLS data, we performed annealing of the

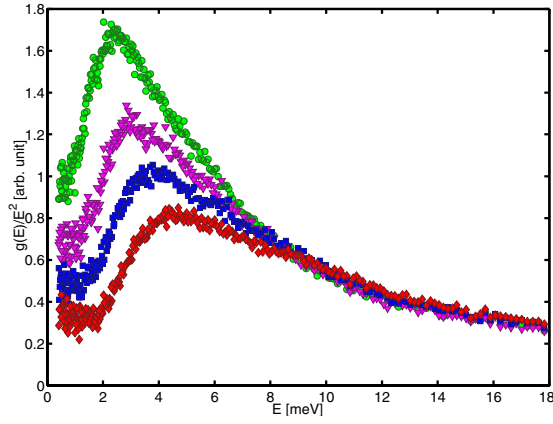


FIG. 1 (color online). The reduced vibrational density of states $[g(E)/E^2]$ obtained by INS, of PIB at different pressures: atmospheric pressure (●), 0.4 (▼), 0.8 (■), and 1.4 GPa (◆).

sample (2 hours at $T = 430$ K) at the highest pressure and then slowly cooled it down to 140 K. The BLS results differ less than $\sim 4\%$ from the ones obtained without annealing. Ruby fluorescence was used to estimate the pressure in the cell (accuracy ± 0.05 GPa). Longitudinal V_{LA} and transverse V_{TA} sound velocities were calculated from the frequencies of the corresponding Brillouin peaks.

The INS data were corrected using a standard procedure (ILL-INX program). The data were normalized to the integral of the elastic peak, which eliminates the effect of the pressure-dependent Debye Waller factor as well as the pressure-dependent number density. The resolution function measured at 2 K had a small wing up to about 2 meV (due to the high pressure cell) and has therefore been subtracted. The data measured over the Q range from 5 to 40 nm^{-1} were corrected for the temperature Bose factor and summed in order to obtain the vibrational density of states $g(E)$. No correction for multiple scattering was performed.

The INS spectra show a strong decrease in the boson peak amplitude and an increase in its frequency under pressure (Fig. 1). The IXS data were fitted using the damped harmonic oscillator model (DHO). The results demonstrate that the whole dispersion curve for the longitudinal sound waves becomes steeper under pressure (Fig. 2). The sound velocity estimated at $Q = 2 \text{ nm}^{-1}$ agrees well with the BLS data, suggesting a linear dispersion up to high Q . The shift of the IXS mode under pressure follows the shift of the LA mode in BLS (Fig. 2), suggesting that the longitudinal sound velocity varies the same way for all of the modes even in the energy range of the boson peak [18].

A comparison of the frequency variation of the different modes demonstrates that pressure affects the boson peak more strongly than any sound mode and, consequently, the Debye level [Fig. 3(a)]. Using the equation of state [19], we estimated that for PIB the density changes with pressure by 20% at $P = 1.4$ GPa. Defining the Grüneisen parameter as $\gamma = d \log(E_{\text{peak}})/d \log \rho$, we estimate $\gamma \sim 2.7$ for the LA

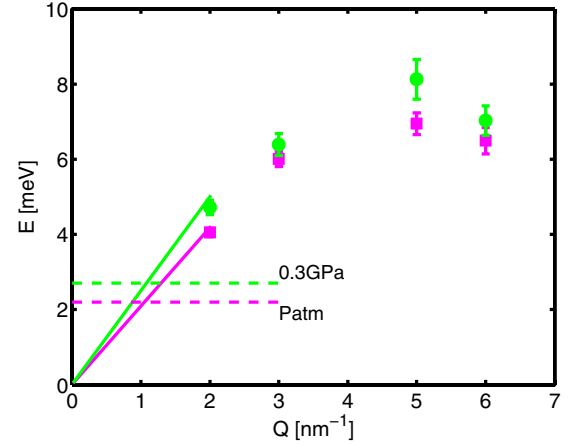


FIG. 2 (color online). The dispersion of longitudinal sound modes measured by IXS at P_{atm} (■) and 0.3 GPa (●). Solid lines: Linear dispersion corresponding to the low Q sound speed measured by BLS. Horizontal dashed lines: Position of the boson peak at the same pressures.

modes and $\gamma \sim 3.7$ for the boson peak. This result is in clear contradiction with a recent analysis of densified $\text{Na}_2\text{FeSi}_3\text{O}_3$ glasses [15]. The authors concluded that variations of the boson peak can be fully described by the transformation of the elastic continuum. We find for PIB that the variations of the boson peak frequency are clearly stronger than the frequency change of the sound modes [Fig. 3(a)]. Our observation is consistent with earlier studies of oxide glasses [6] where changes of the boson peak frequency in Raman spectra under pressure were stronger than variations of the sound velocities. A possible origin for this controversial result may be found in the rather different density variation, amounting to only $\sim 6\%$ in Ref. [15], compared to $\sim 20\%$ here. Another reason for the different result could be that the NIS experiment [15] probes only a part of the density of states, while neutrons better reflect the total $g(E)$.

Let us now turn to the analysis of the variation of the boson peak amplitude I_{BP} [Fig. 3(b)]. It decreases more than 50% at $P = 1.4$ GPa. The usual interpretation of this decrease is a suppression of the excess vibrational modes under compression of a glass [14]. This decrease, however, should be compared to the variations of the Debye density of vibrational states $g_{\text{Deb}}(E)$. The Debye model assumes an isotropic homogeneous elastic continuum and predicts

$$g_{\text{Deb}}(E) = \frac{3E^2}{E_{\text{Deb}}^3}, \quad \text{where} \quad \frac{1}{E_{\text{Deb}}^3} = \frac{1}{18\pi^2 \hbar^3 N} \left(\frac{1}{V_{\text{LA}}^3} + \frac{2}{V_{\text{TA}}^3} \right),$$

where N is the number density. We compare the relative variations of the boson peak amplitude and of $g_{\text{Deb}}(E)$ [Fig. 3(b)] to exclude any errors coming from estimates of the absolute values. The analysis shows that the Debye density of states actually decreases more strongly than I_{BP} . The estimated error for $g_{\text{Deb}}(E)$ is $\sim 10\%$ mostly due to the accuracy of the pressure measurements in BLS experi-

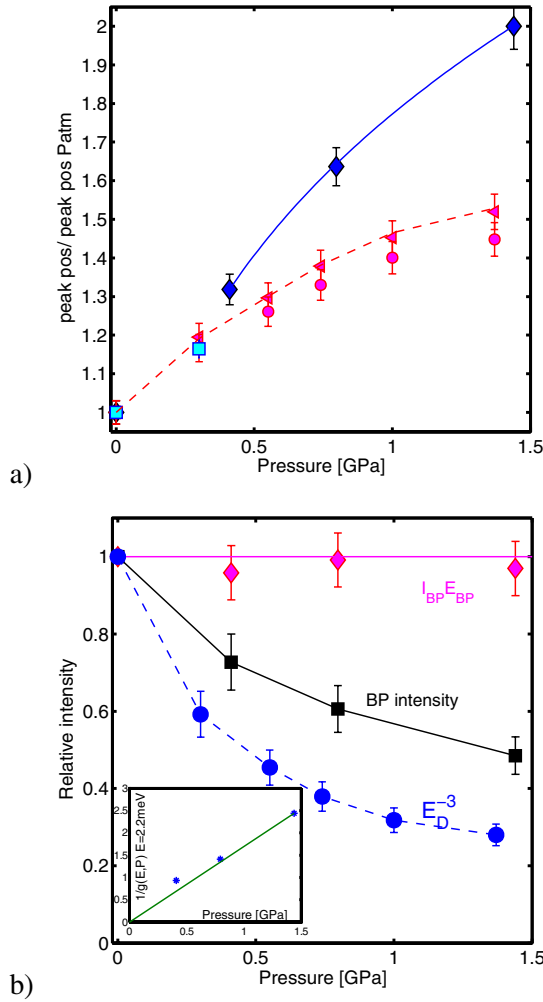


FIG. 3 (color online). (a) The relative shift in energy as a function of pressure. Boson peak (\blacklozenge), BLS longitudinal modes (\blacktriangleleft), BLS transverse modes (\bullet), IXS longitudinal modes (\blacksquare). The solid line represents a $P^{1/3}$ fit of the higher pressure values of the boson peak energy and the dashed line the relative changes with P of the E_{Debye} . (b) The Debye level (\bullet) and the boson peak intensity (\blacksquare) as a function of pressure, and the product of the boson peak intensity and boson peak energy $I_{\text{BP}}E_{\text{BP}}$ (\blacklozenge). Inset: Pressure dependence of the amplitude $1/g(E, P)$ at a fixed frequency 2.2 meV on the left side of the boson peak.

ments. Within this error, the boson peak amplitude decreases under pressure less than the Debye level [Fig. 3(b)]. This result clearly indicates that the boson peak amplitude relative to the Debye level actually increases, at least in the case of PIB. It is interesting to note that the observed change in the amplitude I_{BP} seems to be inversely related to the observed shift of the boson peak E_{BP} , and the product $I_{\text{BP}}E_{\text{BP}}$ does not change as a function of pressure [Fig. 3(b)]. This relationship differs from the one expected in a simple Debye model $g_{\text{Deb}}(E)/E^2 \propto E_{\text{Deb}}^{-3}$, suggesting that it is not a simple elastic continuum transformation.

Comparison of the spectral shape of the boson peak reveals a surprising result (Fig. 4): Despite the increase

of the boson peak frequency to almost twice and decrease of its amplitude to less than half its initial value, the distribution of modes remains identical and independent of pressure or density. No change in the spectral shape of the boson peak has been also reported for quenched [20] and densified [15] glasses. This invariance of the boson peak spectrum under such strong compression indicates that separating the vibrations in this frequency range into acoustic modes and quasilocal excess vibrations is not appropriate. Apparently, all of these modes are coupled and hybridized, forming a universal distribution of the vibrational modes that is not affected even by 20% densification of the glass.

We compare now our results to predictions of different models. In the soft potential model (SPM) [21], the frequency of the boson peak is determined by the strength of the random force f_0 between quasilocalized vibrations $E_{\text{BP}} \sim f_0^{1/3}$. Hydrostatic pressure P will, in a linear approximation, lead to an increase of this random force according to $\delta f = P\Lambda/3K$, where Λ is a random deformation potential of the quasilocalized vibration and K is the bulk modulus at atmospheric pressure [22]. As a result, $E_{\text{BP}} = E_{\text{BP},0}(1 + P/P_0)^{1/3}$, where $P_0 = Kf_0/\Lambda_0$. At large P , $P \gg P_0$, assuming other parameters, in particular K , are pressure-independent, one has $E_{\text{BP}} \sim P^{1/3}$. At such pressure, the amplitude of the boson peak on the left side of the peak depends on pressure at fixed frequency as $1/P$. Our experimental data are in good agreement with these predictions of SPM (Fig. 3). However, the dependence of K on P is not negligible in our case; e.g., K in the glassy state at $P = 1$ GPa is ~ 2.5 times higher than at ambient conditions. It is not clear why the theory with constant elastic moduli works surprisingly well at such high pressures. We note also that SPM predicts the mentioned above rule $I_{\text{BP}}E_{\text{BP}} = \text{const}$. Indeed, in SPM, the density of states is $g(E) = AE^n$, with $n = 4$ on the low-frequency side of the boson peak and $g(E) = BE$ on the high-frequency side,

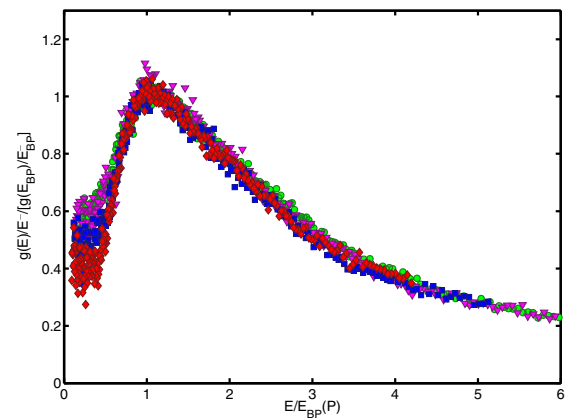


FIG. 4 (color online). The boson peak at different pressures: atmospheric pressure (\bullet), 0.4 (\blacktriangledown), 0.8 (\blacksquare), and 1.4 GPa (\blacklozenge). The data from Fig. 1 scaled with the boson peak intensity and the boson peak position.

where A and B are some constants and B is claimed to be independent of pressure [21]. One can show that, in this case independently of A and n ($n > 2$), $I_{BP}E_{BP} \sim B$ and thus is pressure-independent.

There are no explicit predictions regarding the influence of pressure on the boson peak in other models. Models based on phonon localization in nanoscale domains (blobs) [3,6,23,24] yield to the relationship $E_{BP} \propto V/L$, where V is the sound velocity and L is the size of the blobs that is not well defined. In the framework of these models, variations of E_{BP} stronger than V [Fig. 3(a)] would indicate a significant (30%) decrease in the characteristic size under pressure. This conclusion agrees with the recent theoretical predictions [25,26] that the correlation length associated with the boson peak should decrease with an increase in density. The recent model of Schirmacher and co-workers [27] relates the BP to the fluctuations of elastic constants that scatter sound waves and cause a change in their $g(E)$. It predicts that the boson peak position shifts to higher energies (relative to the Debye frequency that was assumed to be constant) if the amplitude of the elastic constant fluctuations decreases. An increase of the boson peak energy should be accompanied by a decrease in the boson peak amplitude with respect to the Debye level. In general, we expect that pressure can reduce the structural fluctuations and according to the model [27] should lead to a shift of the boson peak and to a decrease of the boson peak intensity relative to the Debye level. Although we observe the predicted shift, such a decrease is not found in the evolution of the boson peak intensity. Recent modification of the theory [28], however, suggests that the shift of the boson peak position without change of its amplitude (everything scaled by the corresponding Debye values) may be observed in some range of parameters.

To conclude, we studied variations of the vibrational spectra of a polymeric glass under the highest level of densification (20%) ever achieved in such measurements. The detailed analysis of the data obtained by three different techniques demonstrates that under pressure (i) the boson peak position shifts more strongly than any sound mode, (ii) the intensity of the boson peak relative to the Debye level does not decrease and even slightly increases, and (iii) the spectral shape of the boson peak remains unchanged and the product $E_{BP}I_{BP}$ remains constant. These results clearly indicate that changes in the boson peak cannot be ascribed to a suppression of the low-frequency modes; it is rather a shift of the vibrations to higher frequency due to hardening of the structure under compression. The changes, however, cannot be explained by a simple deformation of the elastic continuum. The results also suggest that a separation of the vibrational density of states into Debye-like sound waves and into excess modes is questionable in this pressure range. The observed independence of the scaled spectral shape on pressure suggests that all of the modes form a universal distribution and change in a similar way under compression.

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