Probing the different spatial scales of Kel F-800 polymeric glass under pressure

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Glass forming systems, exhibit unique universal characteristics related with the absence of a long-range order. Among them, the low frequency broad peak in the Raman spectra, the Boson peak (BP) and the first sharp diffraction peak (FSDP) in x-ray and neutron diffraction patterns are considered to be related to the disordered nature of these materials1–3.

Despite numerous experimental and theoretical studies over the past decades, the scattering mechanism responsible for the BP is still a matter of debate and controversy4–7. However, it is generally concluded that the BP spectrum involves vibrations of the disordered solid beyond the atomic distance scale. In inorganic network glasses, this scale has been suggested to represent the medium-range order (MRO) of the glasses4–7. The FSDP in network glasses has also been associated with the MRO8. As in the case of the BP the precise origin of FSDP and its relation to the structure of glasses remains controversial8–12. Among the various interpretations for its origin, two have attracted most of the attention in the case of covalent network glasses (mainly chalcogenide and oxide glasses): a) the FSDP is a consequence of the partial periodicity (order) of the MRO (cages) existing in the glass13 and b) it is due to the chemical ordering of interstitial voids around cation centered clusters8. On the other hand, for elemental glasses such as Se, S and amorphous red P FSDP has been attributed to the existence of disordered rings (Se6 and S6) and/or chains14, while FSDP of metallic glasses is believed to arise from the presence of atomic clusters, quasicrystal-like, connected via a fractal network15.

In the case of polymer glasses, the term structural correlation length is used to describe the correlation between polymeric chains. The so-called polymerization (or van der Waals) peak represents real space distances consistent with the expected inter-backbone distances16 and so is the analogous feature of the FSDP peak. Hence, hereafter we will refer to this as FSDP for either network or polymer glasses. Additionally, main (backbone) and side chains are expected to contribute to the long wavelength vibrations and BP may be related to fluctuations (density or elasticity) between the space field with backbones and side chains of the polymer.

Several approaches have been made to establish a correlation between the BP and the FSDP1,2,17–19. A possible universal correlation would be a general feature of amorphous solids, independent of specific structures and bonding. It might also clarify the issue about a possible correlation between the origin of the low frequency excitations (BP) and the structural characteristics of glasses. Diverse proposals have been reported in the recent literature: a) supporting a simple relation between them1,17,19 b) questioning the previous concept of a simple relation with the suggestion of a more complicated relation2,18 and c) completely rejecting any relation between BP and FSDP. Therefore, the relation, if any, between FSDP and BP is a matter of an open strong debate. The intensity and the position of both features are known to vary with temperature and pressure1. It is well known, from both Raman scattering20 and x-ray diffraction19 measurements, that MRO is more strongly affected by pressure than the short range order (SRO). This is directly related with the large free volume of glasses that results to a higher compressibility of glasses compared to the crystalline counterparts, since SRO is practically the same. Hence, the
pressure behavior of both features will aid in our understanding the BP and FSDP and possible relationships between them.

In a theoretical study using the soft-potential model (SPM), Gurevich et al.\textsuperscript{21} have proposed the following expression for the frequency of the BP as a function of pressure:

\[
\omega_b(P) = \omega_b(0) (1 + P/P_0)^{1/3}
\]

where \(\omega_b(0)\) is the BP frequency at ambient pressure and \(P_0\) is a parameter proportional to the ambient-pressure bulk modulus \(K_0\) of the glass. Although equation (1) represents a simple phenomenological approach, its prediction is in good overall agreement with in situ Raman BP data for several network glasses\textsuperscript{19,22,23}, in which there is no significant variation of \(K\) with pressure. In contrast, significant deviations from equation (1) have been found\textsuperscript{24} for polymer glasses because of the strong pressure dependence of their bulk modulus. Recent theoretical studies (e.g. Ref. 25), aimed to provide exact equations, are still in an early stage and therefore could not be used towards a direct comparison with experimental findings. As for the FSDP, the quantitative pressure behavior is still not well understood. In the past, very few studies have attempted to record in situ both the BP and FSDP features under pressure, mainly due to experimental difficulties associated with the recording of BP inside a diamond anvil cell (DAC). To the best of our knowledge, only for \(\text{SiO}_2\) a simple empirical relation between BP and FSDP was suggested\textsuperscript{17,19}, which were in contrast with each other. In addition the true underlying nature of these relations, i.e. the correlation between the origins of the two features, was not examined.

In this work we present a detailed \textit{in situ} high-pressure study of both FSDP and BP for a polymer glass, namely Kel F-800. The results are combined and analyzed along with pressure-dependent sound velocities data reported previously\textsuperscript{26}. Our aim is twofold: a) to provide further input to the debate about a possible correlation between the two features through comparisons of their pressure dependence and b) to test if the existing models for the origin of BP are in agreement with experimental findings.

**Results**

Representative Raman spectra of the Kel F-800 polymeric glass as a function of pressure are shown in Fig. 1(a). As in previous studies\textsuperscript{19,22–24} the BP hardens with pressure and this is accompanied by a decrease of its intensity. The pressure dependence of the BP frequency \(\omega_b\) (Fig. 2) deviates from the theoretical predictions at high densities. Presumably this behavior is due to the large increase of bulk modulus with pressure for this glass, which amounts to nearly an order of magnitude by 14 GPa\textsuperscript{26}.

Fig. 1(b) shows the x-ray diffraction patterns of Kel F-800 glass with increasing pressure. As in the case of the BP, the intensity of the FSDP decreases with pressure. With increasing pressure the position of the FSDP \(Q_1\) increases in qualitative agreement with all previous reports (e.g. Ref.19) for different types of glasses.

As already mentioned, several studies have related the BP frequency to a characteristic dynamical length \(R\) (correlation length).
The physical meaning of $R$ varies in different models. For instance $R$ may be: (i) a cluster size inside the glass\(^{36}\), (ii) the scattering localization length due to density, elastic or elasto-optic property fluctuations\(^{28,29,30}\), and (iii) the length of propagation of high-frequency stress\(^{30}\). Independently from the proposed model $\omega_b$ can be related to $R$ through a simple equation\(^{28,31}\)

$$\omega_b \approx A \frac{V_s}{R}$$

where $V_s$ is the sound velocity, and $A$ is a constant depending on the particular model. Equation (2) represents the expected phenomenological relation between $\frac{1}{R}$ and the inverse of a dynamical characteristic length. Here we use equation (2) in the form $\omega_b \approx \frac{V_s}{2cR}$ where $c$ is the speed of light. Previous studies\(^1\) have shown that, although $\omega_b(0)$ may vary from 10 to 200 cm$^{-1}$ for different glasses, $R$ usually takes values in a narrow range of 1 to 2 nm. This implies that $\omega_b(0)$ is mainly defined by the elastic constants. Although equation (2) is not an exact equation and “microscopic” sound velocities with nm wavelengths should be used\(^{35}\), it provides a simple and straightforward prediction about the $R$ trend under pressure. Moreover, it is difficult to obtain “microscopic” sound velocities under pressure, and this is why this equation was used by most of the previous studies.

Normalized sound velocity $V_s(P)/V_s(0)$ from\(^{26}\) as a function of pressure is plotted in Fig. 2. The pressure behavior of $V_s(P)$ is broadly similar to that displayed by $\omega_b$, but the overall increase is almost doubled ($\omega_b(P_{max}) = 1.9 \omega_b(0)$ vs $V_s(P_{max}) = 3.9 V_s(0)$). Therefore, the rate at which the BP hardens with pressure lags considerably the stiffening of the elastic medium. It appears that the relation between the rate of increase of $\omega_b$ and $V_s(P)$ with pressure is not the same for all glasses (see Ref.\(^{24,33}\)). According to equation (2), this means that $R$ should increase with pressure in contrast to the previously reported experimental results for other polymers\(^{24}\) and also contrary to the expectation of the structural models of BP\(^{27}\) as one expects a decrease of the MRO structural dimensions under pressure.

### Discussion

From equation (2) we have calculated the inverse correlation length $1/R$ values using $\omega_b$ values from this study and $V_s$ values from Ref.\(^{26}\) (Fig. 3). Fig. 3 also shows the FSDP peak position $Q_1$ plotted as a function of pressure. It is clearly seen that $1/R$ decreases with pressure (rapidly during the first step of compression), while the FSDP shifts to higher momentum transfers. The latter implies a decrease of the inter-backbone characteristic structural dimensions\(^1\). This is not compatible with the increase of $R$, if we consider the structural models of BP. $R$ may be also attributed to a dynamical scattering length (localization length) which, according to the Ioffe–Regel condition, is the phonon’s wavelength when equal to phonon’s mean free path\(^{36}\). Another point of view is to attribute $R$ to the crossover point between the phonon thermalization length and the propagation length due to elastic properties fluctuations\(^{36}\). In this case, the increase of $R$ under pressure means that the phonon localization length increases.

This is in favor of the various proposed fluctuation models of BP. Thus, BP and FSDP probe different spatial scales, i.e. structural dimensions in the case of FSDP and fluctuation dimensions for BP. The increase of $R$ with pressure may be interpreted as the result of the free volume decrease and a consequent “homogenization” of the intermediate range structure of the glass, i.e. limited density or elastic fluctuations and a decrease of topological disorder. It is generally known\(^{37}\) that the BP relative intensity increases with increasing disorder for a given glass. Since the decrease of the BP intensity with increasing pressure is a universal observation\(^{1,3}\), it may also be related with the increase of $R$ (decrease of disorder). In a previous study on GeO$_2$ glass, a similar analysis between BP and $V_s$ has been used by Deschamps et al.\(^{38}\). They concluded that the decrease of BP intensity is related to the anomalous softening of the elastic moduli, in a narrow pressure interval, and the consequent increase of $R$ due to the elastic homogenization. Moreover, a similar interdependence between $1/R$ and BP intensity was also observed by Levelut et al.\(^{19}\) around the glass transition.

Here we concentrate on possible correlation between BP and FSDP using the pressure behavior of these two features. The first proposed\(^1\) and simplest relation between BP and FSDP is in the form $1/R \sim Q_1$. This relation is based on the assumption that $R$ represents an effective size of the clusters. Although this relation holds relatively well for different glasses at ambient conditions\(^1\), it is obvious from Fig. 3 that it fails when applied to KeF-800 glass under pressure. In another approach\(^1\) the relation $R \sim 1/AQ_1$ has been proposed, where $AQ_1$ is the width of the FSDP. This relation was based in the hypothesis that the Scherrer equation for microcrystalline samples, also holds for glasses. However, the available experimental data (including those of the present work) do not show any substantial decrease of $AQ_1$ with pressure.

Apart of the above mentioned generally proposed relations between BP and FSDP there has also been further number of attempts to relate their pressure dependencies. Sugai and Onodera\(^{17}\) suggested an empirical relation in the form $\omega_b \sim V_s/AQ_1$ which is compatible with the $R \sim 1/AQ_1$ one. They found that there is a linear relation between $\omega_b$ and $AQ_1$. In this event, $V_s$ should be constant under pressure, in contrast to all previously reported results. Elsewhere, Hemley et al.\(^{19}\) and Inamura et al.\(^{39}\) proposed a linear relation between $\omega_b(P) - \omega_b(0)$ and $Q_1(P) - Q_1(0)$ based on $1/R \sim Q_1$ relation. This result has been attributed in Ref.\(^{40}\) to the fact that the increase of $\omega_b$ means that $R$ decreases and so that the relation $1/R \sim Q_1$ is fulfilled. However, this conclusion is not valid for the glass of this study since $R$ effectively increases with pressure.

Although a near linear relation $\omega_b \sim Q_1$ can be valid under pressure (see inset of Fig. 3) it may not reflect the true correlation between $\omega_b$ and $Q_1$.
with the high compressibility of the Kel F-800 polymer glass. 

These proposals are schematically backbones for a polymer) decreases, however the dynamical correlation length (distance between backbones for a representative polymer). The dimensions of the structural (d) and scattering (R) correlation lengths are indicated with arrows.

BP and FSDP. Our results suggest that the correlation length (see equation (2)) is the main factor that affects frequency and intensity of the BP, since V_s is a bulk property. Consequently, we propose that under pressure the structural correlation length (distance between backbones for a polymer) decreases, however the dynamical correlation length increases due to “homogenization”. The latter is consistent with the BP intensity decrease. These proposals are schematically illustrated in Fig. 4. At low pressures the distance between backbones is large because of the voids created from the side chains. With increasing pressure the free volume decreases and backbones approach each other. This compression mechanism is in agreement with the high compressibility of the Kel F-800 polymer glass. According to this, the density and/or elasticity fluctuations becomes less influential as the void space collapses. Consequently, the dynamical correlation length R increases upon pressure exertion. We conclude that, BP and FSDP are not directly correlated because they probe different spatial scales corresponding to fluctuation and structural dimensions, respectively. Thus, the previously proposed phenomenological relations, although may be valid, are coincidental and doesn’t reflect the actual anticorrelation behavior under pressure between the microscopic characteristic lengths of these features.

Further studies are necessary to confirm the universality of this observation and for better understanding of the simple model we propose here. First, the dynamical correlation length under pressure should be examined for other types of glasses (network and polymeric), in order to better understand the origin of the difference in its properties of a fluorinated copolymer: Poly(chlorotrifluoroethylene-co-vinylidene fluoride) (Kel-F 800).

Figure 4 | Schematic representation of low (a) and high (b) pressure configuration of polymer backbones and voids for a representative polymer. The dimensions of the structural (d) and scattering (R) correlation lengths are indicated with arrows.

Methods

Kel F-800 fluorocarbon polymer is a 3 M copolymer derived from the monomers chlorotrifluoroethylene (CTFE) and vinylidene (VF2). A small piece of Kel F-800 polymer was loaded inside the DAC without any pressure transmitting medium. Small quantities of ruby and gold powder were also loaded, for determination of pressure through ruby luminescence and gold EOS, respectively. Raman spectra were measured with a backscattering geometry using the 532 nm line from a solid state laser for excitation. An experimental setup capable to record Raman spectra at very low wavenumbers (<10 cm⁻¹) using solid state notch filters was used. Diffraction data were collected at the GSECARS (sector 13), using a MAR355 CCD detector. The monochromatic x-ray beam (wavelength λ = 0.3534 Å) was focused to a nominal diameter of 4 μm. For this glass Tm = 307 K at ambient pressure, and is expected to increase with pressure. Raman experiments were performed at room (293 K) and at low temperature (278 K) well below Tm, yielding very similar results for the BP position, but BP is much better resolved at low temperatures.

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**Author contributions**

E.S. and A.G designed research. E.S. M.A. and A.G. conducted the experiments. All authors reviewed the manuscript.

**Additional information**

**Competing financial interests:** The authors declare no competing financial interests.

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CORRIGENDUM: Probing the different spatial scales of Kel F-800 polymeric glass under pressure

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The authors have noticed that in the original version of this Article, in the discussion section, there was a sentence that may result to a misinterpretation of previous results. They would like to clarify that Deschamps et al. (Ref. 38) showed that the “typical size D of the elastic cohesive domains” decreases with increasing pressure. In this study by Stavrou et al., R represents the dynamical correlation length and so, the statement that R increases under pressure was based on the authors’ model.