

Pressure Evolution of the Excess Wing in a Type-*B* Glass Former

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Glass formers are defined as “type *B*” when they exhibit a distinct Johari-Goldstein (JG) relaxation, but lack an excess loss (“excess wing,” EW) in their structural relaxation peak. By studying the dielectric spectra of a well-known type-*B* glass former under high pressure, we unequivocally show the existence of an EW, simultaneously with the JG relaxation. Moreover, at very high pressures (0.6 GPa), the EW becomes a distinct relaxation peak, although correlated with the structural relaxation. The implication is that the EW, rather than the higher frequency relaxation ascribed to the JG process, is perhaps a universal feature of glass formers, albeit not always discernible at ambient pressure. Our findings may reconcile all opposing points of view present in the literature, as well as indicate that the type-*A* or type-*B* classification of glass formers should be modified or even discontinued.

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The number of models of the glass transition seems to be inversely proportional to the degree to which any one can provide a completely satisfactory description of the vitrification phenomenon. This unsettled state of affairs is not the consequence of a lack of research effort, but rather reflects the complex dynamics of supercooled glass formers. On approaching the glass transition from above, liquids undergo a strong, progressive increase of viscosity, attaining values so high that the material behaves as a solid, yet retaining the microscopic disorder of the liquid phase. This is accompanied by an increase in the characteristic time for molecular motions from values on the order of the nanoseconds to time scales exceeding feasible experimental durations.

The dielectric spectra of glass formers reveal multiple relaxation processes. Most prominent is the structural, or α , relaxation, whose behavior is coupled to the viscosity, and has a characteristic time, τ_α , which diverges below the glass temperature (T_g). In type-*B* glass formers, there occurs a faster, secondary relaxation, often referred to as the Johari-Goldstein (JG) relaxation [1,2], and characterized by activated dynamics for temperature below T_g , that if extrapolated to high temperature seems to merge with the α peak at a temperature about $1.2T_g$ [3]. In some glass formers, known as “type *A*”, the JG peak is absent in the dielectric spectrum, but there is an extra loss on the high frequency side of the α dispersion. This excess loss, called the “excess wing” (EW), exhibits power law behavior with an exponent smaller than that describing the high frequency flank of the α relaxation. It is commonly believed that type-*B* liquids lack an excess wing, which gives rise to an ongoing debate of whether the EW is a submerged JG peak, or an inherent feature of the α relaxation. The latter hypothesis is supported by an appropriate scaling [4], although this sometimes fails [5,6]. Moreover, in some liquids the EW can be transformed into a shoulder (nascent peak) by physical aging [7,8]. The fact that the EW may not be an inherent part of the α

relaxation does not necessarily mean that it is a JG relaxation. In fact, measurements at high pressure indicate that the pressure dependence of τ_{EW} is nearly the same as that of the α peak [9–12], whereas τ_{JG} exhibit a much weaker pressure dependence [9,13,14], implying that the two processes are distinct.

One means used to demonstrate the “equivalence” of the EW and JG is from measurements on a series of chemically identical materials, varying only in molecular weight. With increasing chain length, the JG becomes progressively less separated from the α relaxation, eventually merging into an EW. Three studies of this type have recently been reported, on polypropylene glycol (PPG) [15], polyalcohols [16] (glycerol, threitol, xylitol, and sorbitol) and PPG-based dimethyl ethers [17]. In each case, the same conclusion was reached, that the EW is merely an unresolved JG. This suggests that the distinction between type-*A* and type-*B* glass formers is not fundamental, but only reflects the experimental conditions used for a particular measurement.

In light of these provocative findings, it is of interest to investigate the effect of pressure on the JG in PPG oligomers, given the differing sensitivity to pressure of the JG and EW [9–14]. If the EW is in fact a JG, we expect that: (i) the JG will become more pressure sensitive for shorter chain lengths, (ii) the JG and α peaks will progressively separate with increasing pressure, and (iii) an EW will never be observed in the presence of a JG peak. However, if the EW is actually distinct from the JG process, the τ_{JG} will hardly change with pressure, offering the possibility that both processes (EW and JG) might be observed in the same spectrum. Note that due to the breadth of the α dispersions and their poor separation at ambient pressure, this undertaking requires measurements at very high pressure. To our knowledge, perhaps the only existing study supporting the coexistence of EW and JG relied on derivatives of the dielectric loss measured at ambient pressure, and not the spectra *per se* [18].

Herein, we present data for the PPG terpolymer (Tri-PPG, from Aldrich), for which $M_w = 188$ kg/mol and $T_g = 193$ K. Previous results on the JG and α relaxations of this material at atmospheric pressure were reported in Ref. [15], while one of the first discussions regarding the JG in a high polymer of PPG can be found in Ref. [19]. Broad band dielectric measurements covering 10 decades of frequency were carried out using two high resolution dielectric instruments, an Imass Time Domain Dielectric analyzer (10^{-4} – 10^3 Hz) and a Novocontrol Alpha Analyzer (10^{-2} – 10^6 Hz). The spectra were measured up to pressures of about 0.6 GPa, at temperatures as low as 220.5 K. Details on the experimental setup and a more extensive presentation of this study will be published subsequently [20].

Three representative dielectric loss spectra, ϵ'' , for atmospheric pressure are shown in Fig. 1, one measured at T_g and the other two at lower temperature. Included in the figure is the Kohlrausch-Williams-Watts [21,22] (KWW) fit, with $\beta_{\text{KWW}} = 0.63$. This same value of the stretch exponent, independent of temperature, was reported previously [15]. From the spectra in Fig. 1, no EW is clearly evident, because of the proximity of the JG relaxation. However, some deviation from the KWW power law can be noted in the high frequency flank of the α peak. In the inset to the figure is shown a master curve, constructed by shifting along the abscissa the two lower temperature spectra by a factor that superimposes the data at lower frequencies. The extended range of the inset provides a stronger suggestion of the presence of an EW.

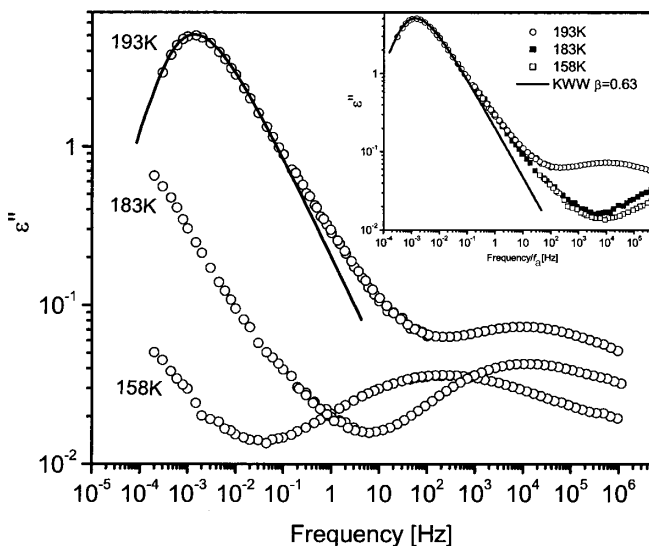


FIG. 1. Dielectric loss spectra for Tri-PPG at atmospheric pressure, at the three indicated temperatures. The solid line is a KWW function with $\beta = 0.63$. In the inset, the same spectra are shown after shifting in frequency to superimpose the high frequency flank of the α relaxation.

In Fig. 2 are the dielectric loss spectra of Tri-PPG at $T = 220.5$ K for different pressures. At low pressure, only the conductivity (not shown) and the α relaxation are present. At higher pressure (ca. 300 MPa), as the α peak slows down, the JG process appears at higher frequency. Further increases of pressure, up to 600 MPa, have little effect on the position of the JG. However, an EW becomes clearly visible on the high frequency flank of α relaxation, coexisting with the other two relaxations. At pressures around 500 MPa, the α relaxation is so slow that its contribution in the measured range becomes negligible, whereupon the EW assumes the form of a distinct peak. Thus, these spectra show that the EW can be completely separate from the JG relaxation. Of course, this coexistence is observed only below T_g , since above T_g the strong intensity of the other two processes makes the EW indistinguishable.

The spectra below T_g reported in Fig. 2(a) were analyzed using a Cole-Cole [23] relaxation function to describe the EW and JG, and a Havriliak-Negami [24] function for the α relaxation. For the spectra at higher pressures, where only the high frequency side of the α relaxation is present, a power law was used. Above T_g , the masking of the EW by the other two relaxations precludes deconvolution, and only the JG peak was considered. All the fits were carried out simultaneously on both the ϵ' and ϵ'' spectra [Figs. 2(b) and 2(a)], with details of the analysis to be described elsewhere [20].

In Fig. 3 are displayed the τ for the three processes, calculated from the frequency of the dielectric loss maxima ($\tau = 1/2\pi f_{\text{max}}$). Using $\tau_{\alpha}(T_g) = 100$ s, the pressure coefficient of the glass transition is determined, $dT_g/dP \sim 75$ K/GPa. This is somewhat higher than the coefficient for the more strongly hydrogen-bonded polyalcohols, for which $dT_g/dP = 34$ to 40 K/GPa [12,13], but much smaller than the values, $dT_g/dP \cong 160$ – 310 K/GPa, for nonassociated glass formers [25,26]. As seen in Fig. 3, the pressure dependence of the EW is comparable with that of the α relaxation, while the JG relaxation is relatively insensitive to pressure. In terms of activation volumes, $\Delta V [\equiv RT \partial \ln(\tau)/\partial P]$, with R the gas constant], $\Delta V_{\alpha} = 96 \pm 4$ ml/mol, $\Delta V_{\text{EW}} = 49 \pm 5$ ml/mol, and $\Delta V_{\text{JG}} = 1.3 \pm 0.7$ ml/mol, for temperatures near T_g . The last value is comparable to that for JG in sorbitol, $\Delta V_{\text{JG}} \sim 5$ ml/mol [13].

A small activation volume means the relaxation process is insensitive to changes in volume, implying that the volume involved in the motion is small. Therefore, the difference between the activation volumes of the EW and JG reflects a fundamental difference in the nature of these processes, the latter involving more restricted motion than the EW. This result seems consistent with: (i) the detection by ^2H NMR of very restricted motion in materials having a distinct JG, but no such observation in type-A glass formers [27] and (ii) the idea that the JG is a localized process [28]. In conclusion, the results presented

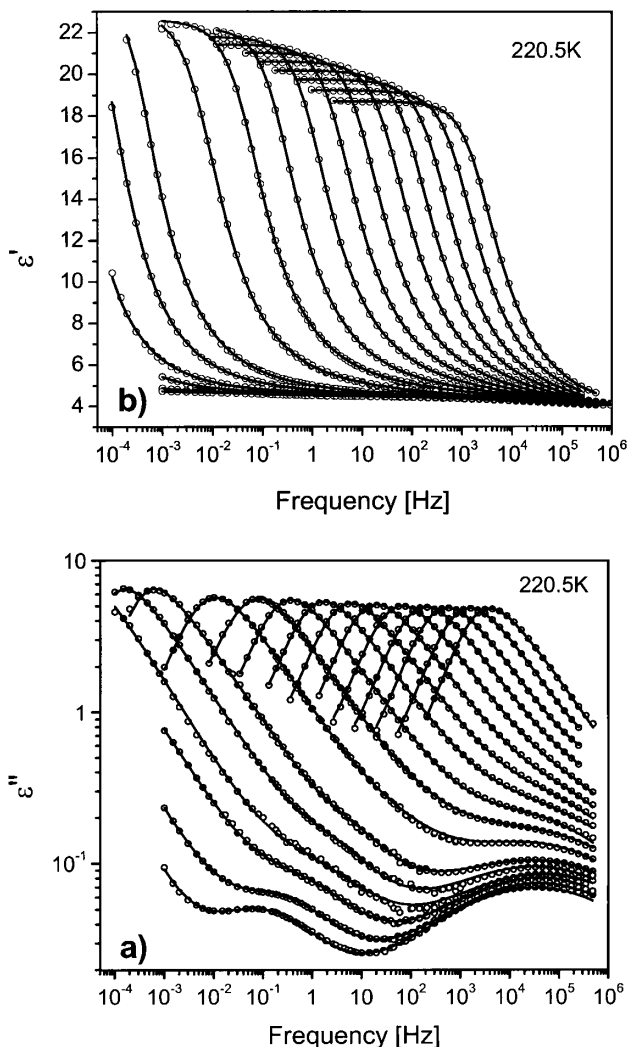


FIG. 2. Dielectric loss (a) and permittivity (b) for Tri-PPG at $T = 220.5$ K, measured at pressures equal to (from right to left): 33.4, 61.9, 93.0, 120.7, 150.0, 180.2, 209.3, 237.5, 268.6, 297.2, 331.3, 373.4, 415.3, 447.2, 463.7, 510.2, and 591.3 MPa. The solid lines are the best fits, as discussed in the text.

herein demonstrate unequivocally that the EW is a secondary relaxation, obscured by the α relaxation. More significantly, the EW is distinct from the secondary relaxation conventionally regarded as the JG. We believe this is the first clear evidence of the coexistence of these two processes; thus, the classification of glass formers as type A or type B loses its meaning. The EW, rather than the higher frequency process often identified as a JG relaxation, may be the real universal property of glass formers. However, additional studies on other glass formers are necessary. Finally, the results herein seem to support the idea that the EW is strictly correlated to the α relaxation, as suggested by the near equivalence of their volume and temperature dependences. This aspect of the behavior, which can be probed using physical aging ex-

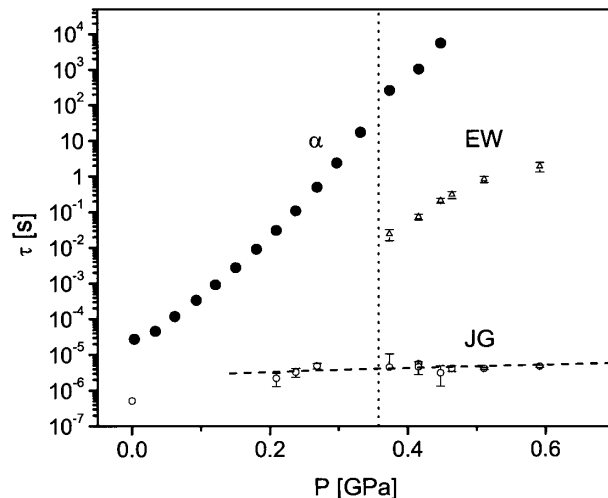


FIG. 3. Relaxation time vs pressure, as obtained from fitting the spectra in Fig. 2. The dotted vertical line indicates the glass transition ($\tau_\alpha = 100$ s). The data point at zero pressure for the JG was extrapolated from the results in Ref. [15].

periments, is an important clue to unraveling the mystery of the vitrification process in liquids.

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