

## Does the Arrhenius Temperature Dependence of the Johari-Goldstein Relaxation Persist above $T_g$ ?

M. Paluch,<sup>1</sup> C. M. Roland,<sup>2</sup> S. Pawlus,<sup>1</sup> J. Ziolo,<sup>1</sup> and K. L. Ngai<sup>2</sup>

<sup>1</sup>*Institute of Physics, Silesian University, ul. Uniwersytecka 4, 40-007 Katowice, Poland*

<sup>2</sup>*Naval Research Laboratory, Chemistry Division, Code 6120, Washington, D.C. 20375-5342, USA*

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Dielectric spectra of the polyalcohols sorbitol and xylitol were measured under isobaric pressures up to 1.8 GPa. At elevated pressure, the separation between the  $\alpha$  and  $\beta$  relaxation peaks is larger than at ambient pressure, enabling the  $\beta$  relaxation times to be unambiguously determined. Taking advantage of this, we show that the Arrhenius temperature dependence of the  $\beta$  relaxation time does not persist for temperatures above  $T_g$ . This result, consistent with inferences drawn from dielectric relaxation measurements at ambient pressure, is obtained directly, without the usual problematic deconvolution the  $\beta$  and  $\alpha$  processes.

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Myriad phenomena transpire as a liquid approaches the glass transition, and these complex dynamics have yet to be entirely characterized, let alone understood. An especially intriguing aspect is the appearance at frequencies higher than the structural  $\alpha$  relaxation of a secondary process, commonly referred to as the Johari-Goldstein (JG)  $\beta$  relaxation. The JG relaxation does not involve intramolecular motion, as demonstrated by its occurrence in rigid molecules [1]. According to Johari [2], structural nonuniformity within the glass leads to “islands of mobility,” which underlie the JG process. In this viewpoint, the JG relaxation is a nonhomogenous process, since it involves only local environments in which molecules are sufficiently free [3]. A distinctly different interpretation is that the process can be attributed to small-angle (and thermally activated) reorientations of all molecules, such motion having a homogenous character [4]. Thus, notwithstanding its central role in the dynamics of supercooled liquids, the fundamental origin of the JG relaxation is a matter of dispute, with much current effort devoted to clarifying its true nature [5–15].

Its intermolecular character and presence in all types of glass formers indicate the potential role of the JG process as the precursor of the cooperative (i.e., intermolecularly coupled)  $\alpha$  relaxation, responsible for vitrification [16]. Such a role of the JG relaxation is also insinuated by its tendency to merge with the  $\alpha$  relaxation above the glass transition temperature,  $T_g$  [17,18]. Estimates of the temperature,  $T_\beta$ , at which the JG relaxation time,  $\tau_\beta$ , becomes equal to the structural relaxation time,  $\tau_\alpha$ , rely on extrapolations of the sub- $T_g$  temperature dependence of  $\tau_\beta$  to temperatures above  $T_g$ . Such determinations are predicated on the assumption that the Arrhenius temperature dependence,  $\tau_\beta = \tau_\infty \exp[E_a/RT]$  (where the prefactor  $\tau_\infty$  and the activation energy  $E_a$  are constants), persists into the equilibrium liquid state. The actual tem-

perature dependence of  $\tau_\beta$  is centrally important to theoretical explanations of the origin of the JG relaxation. However, while the behavior below  $T_g$  is well established, above  $T_g$  the situation is less clear, because of the problem of resolving the JG relaxation from the nearby  $\alpha$  process. An idiosyncratic analysis of dielectric measurements on sorbitol, as well as several other glass formers, led Olsen and co-workers [19] to conclude that near  $T_g$ ,  $\tau_\beta$  becomes invariant to temperature. By analyzing dielectric spectra of sorbitol in this same region by fitting the overlapping  $\alpha$  and  $\beta$  peaks to the sum of two functions, several groups have concluded that the Arrhenius dependence observed

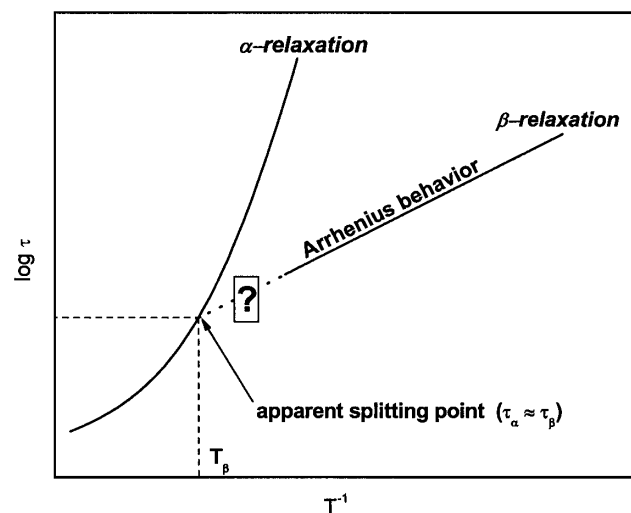


FIG. 1. Schematic illustrating the relationship between the relaxation times for structural relaxation and the secondary process. Extrapolation of the Arrhenius behavior of  $\tau_\beta$  observed below  $T_g$  leads to an apparent merging at  $T_\beta$ ; however, JG relaxation times in the region denoted by the interrogation point have not (heretofore) been measured directly.

below  $T_g$  changes into a stronger temperature dependence above  $T_g$  [20–22]. However, large uncertainty in  $\tau_\beta$  is inevitable in any determination based on the assumption that a single broad peak can be represented in the frequency domain as the superposition of two independent relaxation processes. Thus, the available literature is inconclusive, with a definitive determination requiring the two maxima in the loss spectrum be well resolved above the apparent  $T_\beta$ . The present situation is illustrated schematically in Fig. 1.

The dielectric measurements on sorbitol (also known as *D*-sorbitol) cited above were carried out at ambient pressure [19–22]. In this work, we investigate the JG relaxation in sorbitol under very high pressure, exploiting the large difference between  $\tau_\beta$  and  $\tau_\alpha$  induced by hydrostatic pressure. Better resolution of the JG relaxation allows  $\tau_\beta$  to be determined directly from the spectrum, whereby we show unequivocally that the JG process in

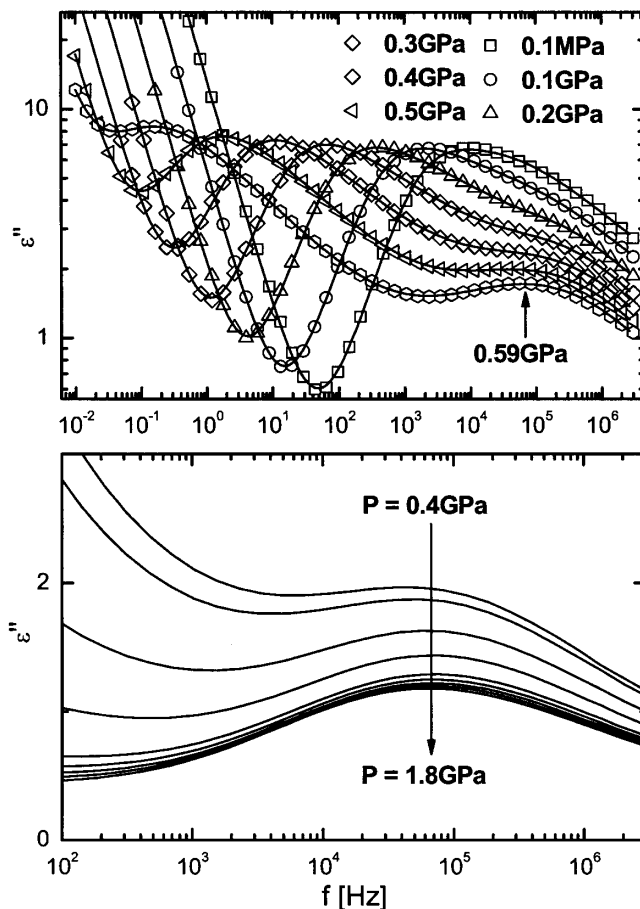


FIG. 2. Dielectric spectra of sorbitol measured at  $T = 293$  K at various pressures from 0.1 MPa to 1.8 GPa. The structural relaxation peak (upper panel) has a strong pressure dependence, as opposed to the secondary relaxation (lower panel) which is invariant to pressure over the range  $0.4 \leq P$  (GPa)  $\leq 1.8$ . Consequently, the initially overlapping peaks are resolved at high pressure.

sorbitol near its structural relaxation peak exhibits two different temperature dependences, changing from one Arrhenius behavior below  $T_g$  to another above  $T_g$ . The invariance to temperature over a narrow temperature range deduced from ambient pressure measurements is not observed at high pressure. These results for sorbitol are corroborated by high pressure dielectric measurements on a second polyalcohol, xylitol. The implication is that the behavior described herein is a general feature of glass-forming liquids.

The samples were purchased from Aldrich and prepared in the manner described in Ref. [10]. Dielectric measurements were carried out in a frequency range from  $10^{-2}$  to  $10^6$  Hz using a Novocontrol Alpha spectrometer. The high pressure technique used herein is very similar to that of Johari and Whalley [23]. Briefly, the liquid sample and the two electrodes forming the capacitor were placed in a Teflon bellows mounted in the high pressure chamber. Hydrostatic pressure was generated by displacing the piston by means of a hydraulic press. This technique enables pressures of a few GPa to be attained.

To verify that compression enables deconvolution of the overlapping  $\alpha$  and  $\beta$  peaks, measurements at  $T = 293$  K were carried out as a function of pressure, in the range from 0.1 MPa to 1.8 GPa. As seen in Fig. 2, while the frequency of the maximum of the secondary relaxation is virtually unchanged, the structural relaxation peak moves toward lower frequency with increasing

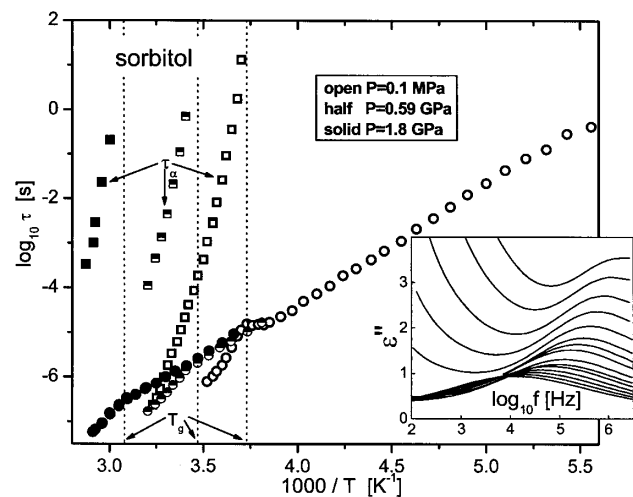


FIG. 3. Isobaric  $\alpha$ -relaxation times at 0.1 MPa ( $\square$ ), 0.59 GPa (half-filled square), and 1.8 GPa pressure ( $\blacksquare$ ), along with the corresponding  $\beta$  relaxation times at ambient ( $\circ$ ) and elevated (1.8 GPa) pressure ( $\bullet$ ) for sorbitol. The slope of  $\tau_\beta$  is independent of pressure, although it differs markedly for low versus high temperatures. The inset shows the JG peak in the dielectric loss at  $P = 1.8$  GPa for temperatures from 273 to 343 K, in  $5^\circ$  increments (bottom to top). The  $\alpha$  peak is too low in frequency to appear within the measured frequency range.

TABLE I. Pre-exponential factor and activation energy for  $J$ - $G$  relaxation in polyalcohols.

	$T < T_g$		$T \geq T_g$	
	$\log_{10}\tau_\infty$	$E_a$	$\log_{10}\tau_\infty$	$E_a$
Sorbitol (0.1 MPa)	$-15.4 \pm 0.1$	$52.8 \pm 0.9$	$-23 \pm 2$	$89 \pm 10$
Sorbitol (1.8 GPa)	$-15.0 \pm 0.3$	$52 \pm 1$	$-20 \pm 0.5$	$85 \pm 2$
Xylitol (0.1 MPa)	$-13.7 \pm 0.6$	$45 \pm 2$	...	...
Xylitol (1.75 GPa)	$-15.0 \pm 0.4$	$53 \pm 3$	$-19 \pm 5$	$77 \pm 8$

pressure. Similar behavior was observed for another polyalcohol, xylitol. Thus, pressure is effective in separating the two relaxation processes.

Representative dielectric spectra of the JG peak in sorbitol measured isobarically at  $P = 1.8$  GPa are shown in the inset to Fig. 3. The clear separation of the JG peak from the  $\alpha$  relaxation enables relaxation times for the former to be determined from the peak frequency. These are displayed in Fig. 3, along with the  $\tau_\alpha$  and  $\tau_\beta$  reported for ambient pressure [20]. At  $P = 1.8$  GPa,  $\tau_\alpha$  falls within our measured range of frequencies only at higher temperatures, whereas at lower temperatures, approaching the glass transition, it is masked by dc conductivity. However, the secondary relaxation process is never obscured by dc conductivity.

At high pressure below  $T_g$ , Arrhenius behavior is found for  $\tau_\beta(T)$ , with an activation energy equal to  $52 \pm 1$  kJ/mol. This is equal to the value determined for ambient pressure,  $E_a = 52.8 \pm 0.9$  kJ/mol. However, for  $T_\beta > T > T_g$ ,  $\tau_\beta$  deviates markedly from this temperature dependence, exhibiting a second Arrhenius region, as seen in Fig. 3. The activation energy at  $P = 1.8$  GPa is equal to  $85 \pm 2$  kJ/mol, which again is equivalent within experimental error to the ambient pressure result for  $T > T_g$ ,  $E_a = 89 \pm 10$  kJ/mol. The large uncertainty in the latter is due to the paucity of data points and their deviation from Arrhenius behavior for  $\tau_\beta = 1.6 \times 10^{-5}$  s. As suggested by Olsen [21],  $\tau_\beta$  appears to become invariant to temperature over a small region around  $T_g$ . However, this anomaly disappears in the compressed liquid. As seen in Fig. 3, at elevated pressure the initial Arrhenius dependence below  $T_g$  segues directly into the second Arrhenius temperature dependence above  $T_g$ . The latter, in addition to a larger  $E_a$ , also has a significantly shorter  $\tau_\infty \sim 10^{-20}$  s (Table I). The fact that extrapolation to high temperature yields an unphysical value of  $\tau_\beta$  (faster than phonon frequencies) indicates that the process cannot continue to high temperatures ( $T \gg T_\beta$ ), but rather merges with the  $\alpha$  relaxation.

This change in temperature dependence of  $\tau_\beta$  is predicted by the coupling model [12,16,24], according to which  $\tau_\beta = t_c^{1-\beta_K} \tau_\alpha^{\beta_K}$ , where  $t_c$  ( $\sim 2$  ps) is a constant and  $\beta_K$  is the Kohlrausch-William-Watts stretch exponent.  $\beta_K$  almost invariably decreases with decreasing temperature for the equilibrium liquid below  $T_\beta$  [25]. Since  $\beta_K$  enters as an exponent in the relation between  $\tau_\beta$  and  $\tau_\alpha$ , this

confers a substantial additional temperature dependence to  $\tau_\beta$ . In combination with the non-Arrhenius temperature dependence of  $\tau_\alpha$ , this is manifested as a higher activation energy. Calculated  $\tau_\beta$  near and above  $T_g$ , using  $\beta_K = 0.48$  [26], are of the same magnitude as the measured  $\tau_\beta$ . Thus, the coupling model can rationalize the  $T$  dependences observed for the JG relaxation time, in addition to predicting the existence of the JG peak present above the extrapolated splitting temperature.

Isobaric dielectric measurements were also made on xylitol at  $P = 1.75$  GPa. Figure 4 displays  $\tau_\alpha$  and  $\tau_\beta$  for ambient pressure [9]. The behavior is qualitatively similar to sorbitol, activated dynamics ( $E_a = 45.3 \pm 1.6$  kJ/mol) below  $T_g$ , with intimation of a leveling off of the  $T$  dependence in the vicinity of the structural relaxation. Overlap with the  $\alpha$  process precludes characterization of the JG process for ambient pressure at higher temperatures, closer to  $T_g$ . The inset to Fig. 4, displaying the loss for several temperatures, makes apparent the separation of the  $\alpha$  and  $\beta$  peaks that is

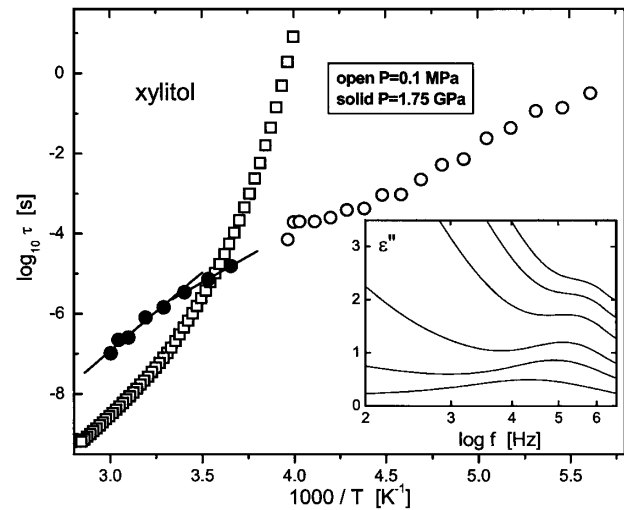


FIG. 4. Isobaric  $\alpha$  relaxation times at ambient pressure ( $\square$ ), along with the  $\beta$ -relaxation times at  $P = 0.1$  MPa ( $\circ$ ) and  $P = 1.75$  GPa ( $\bullet$ ) for xylitol. The  $\tau_\beta$  have almost the same slope below  $T_g$ , but at higher temperatures there is deviation to a larger activation energy. The inset shows the JG peak in the dielectric loss at  $P = 1.75$  GPa for  $T = 283, 303, 313, 323, 328,$  and  $333$  K (bottom to top). The  $\alpha$  peak is toward lower frequency, out of the experimental window.

induced by pressure. From the elevated pressure spectra, we can extract (without deconvolution)  $\tau_\beta$ , and these are also displayed in Fig. 4.

The three distinguishing features identified for the secondary process of sorbitol are likewise seen with xylitol: (i) Below  $T_g$ , the activation energy is hardly changed by an increase in pressure of more than 4 orders of magnitude. (ii) Close to the apparent splitting point, the effect of temperature on the JG relaxation becomes much stronger than below  $T_g$ . (iii) The temperature invariant region inferred from analysis of measurements at ambient pressure is absent at high pressure. These results are collected in Table I.

In summary, high pressure dielectric studies of sorbitol and xylitol reveal the manner in which the  $\beta$  relaxation time evolves beyond the (low-pressure) splitting temperature. The Arrhenius temperature dependence below  $T_g$  changes to a second, steeper (larger  $E_a$ ) Arrhenius temperature dependence above  $T_g$ . However, hydrostatic pressure has no effect on the magnitude of either activation energy. The plateau in the temperature dependence of  $\tau_\alpha$ , apparent at ambient pressure near  $T_g$ , disappears in the compressed liquid. These results provide facts crucial to the formulation of a comprehensive theory, not only of the secondary relaxation process in glass-forming liquids, but of the vitrification process itself.

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