Effect of pressure on the α relaxation in glycerol and xylitol

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The effect of pressure on the dielectric relaxation of two polyhydroxy alcohols is examined by analysis of existing data on glycerol, together with new measurements on xylitol. The fragility, or T_g-normalized temperature dependence, changes with pressure for low pressures, but becomes invariant above 1 GPa. When compared at temperatures for which the α-relaxation times are equal, there is no effect of pressure ($<$1 GPa) on the shape of the α dispersion at higher temperatures. However, nearer T_g, pressure broadens the α peak, consistent with the expected correlation of fragility with the breadth of the relaxation function. We also observe that the α-relaxation peaks for both glycerol and xylitol show an excess intensity at higher frequencies. For xylitol, unlike for glycerol, at lower temperatures this wing disjoins to form a separate peak. For both glass formers, elevated pressure causes the excess wing to become more separated from the peak maximum; that is, the properties of the primary and excess intensities are not correlated. This implies that the excess wing in glycerol is also a distinct secondary process, although it cannot be resolved from the primary peak. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1473652]

I. INTRODUCTION

Among small molecule glass formers, glycerol has received considerable attention.[1–3] Both the dielectric α relaxation and the viscosity of glycerol can be well-described by a single Vogel–Fulcher–Tammann–Hesse (VFTH) equation for temperature below 285 K (α-relaxation times, τ_α, less than $\sim 10^{-9}$ s).[4,5] The crossover temperature, at which τ_α departs from the lower temperature VFTH behavior, roughly coincides with the melting temperature of glycerol, $=$291 K.

Near the glass temperature, T_g, the α relaxation in the dielectric loss spectrum exhibits an excess intensity ("excess wing") at higher frequencies. The molecular origin of this excess contribution is a topic of active research. Experiments of Lunkenheimer *et al.*[6] indicated that the excess wing may be the high frequency flank of the Johari–Goldstein secondary relaxation, partially resolved from the more dominant α peak by means of physical aging. Theoretical support for this interpretation has been proffered.[7] An alternative viewpoint is that the excess wing is an intrinsic feature of the α relaxation, universal for all glass formers. The main argument supporting this idea comes from the scaling of dielectric spectra for various glass formers collected at different temperatures.[8]

The extensive experimental data on supercooled glycerol include measurements at elevated pressure. In pioneering work, Johari and Whalley[9] demonstrated that under isothermal conditions (i.e., varying P at constant T) dielectric relaxation times follow a pressure equivalent of the VFTH equation

$$\tau_\alpha(P) = \tau_0 \exp\left(\frac{D_P P_0}{P_0 - P}\right), \tag{1}$$

where P_0 denotes the pressure at which τ_α diverges, τ_0 is a pressure-independent constant, and D_P, the so-called "strength" parameter,[10] is independent of temperature. An equivalent expression

$$\tau_\alpha(P) = \tau_a \exp\left(\frac{D_P P}{P_0 - P}\right) \tag{2}$$

yields more physically plausible values of the preexponential factor $\tau_a (= \tau_0 \times e^{D_P})$.[9] τ_a denotes the relaxation time at ambient pressure for a given temperature, and thus can be determined directly from measurements at ambient pressure.

Fragility, which refers to the T_g-normalized temperature dependence of either τ_α or the viscosity, is an important parameter for characterizing the relaxation properties of glass formers. Accordingly, interest has been drawn to the effect of pressure on fragility, the latter defined by the steepness index,[11]

$$m \equiv \left(\frac{\partial \log \tau_\alpha}{\partial(T_g/T)}\right)_P\bigg|_{T=T_g} = T\left(\frac{\partial \log \tau_\alpha}{\partial P}\right)_T \bigg/ \frac{dT_g}{dP}\bigg|_{T=T_g}, \tag{3}$$

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where T_g is taken to be the (pressure-dependent) temperature at which the relaxation time assumes an arbitrary values (e.g., 100 s). It is customary to define an activation volume[12]

$$\Delta V \equiv 2.303 \, RT \left(\frac{\partial \log \tau_\alpha}{\partial p} \right)_T,$$ (4)

whereby from Eq. (2)

$$\Delta V = \frac{RT \, D P_0}{(P_0 - P)^2}$$ (5)

and from Eq. (3)

$$m = \frac{\Delta V}{\ln(10) R d T_g / dP}.$$ (6)

Cook and co-workers[13] determined the fragility of glycerol from viscosity measurements at elevated pressure. They reported that the steepness index for the viscosity increased linearly from $m = 55$ at ambient pressure to $m = 160$ at $P = 3$ GPa. This suggests that a liquid of intermediate strength becomes extremely fragile at elevated pressure. However, in determining fragility, Cook et al. had to extrapolate their data over an extended range. In addition, some of the viscosities used for the analysis were measured in the crossover region (near T_m), wherein the reliability of a VFTH-based extrapolation is problematic. Given these limitations, the dramatic effects of pressure on fragility they reported should be verified.

Some years ago, Forsman et al.[14] examined the effect of pressure on the dielectric relaxation of glycerol. They observed that the α-relaxation peak significantly broadens with increasing pressure, in agreement with other investigators.[9] However, no attempt has been made to compare isothermal and isobaric data at ambient pressure. Such a comparison is necessary to ascertain whether the increase of fragility with pressure reported by Cook et al.[13] is associated with an increase of the nonexponentiality of the relaxation function. A correlation between these variables is well established for many glass formers, both molecular and polymeric.[11,15]

In this paper, we examine existing dielectric data on glycerol, using the combined results of various authors,[9,14,16] to address three salient issues: What is the effect of pressure on fragility? Is the correlation between fragility and nonexponentiality maintained under high pressure? And, does the influence of pressure on the dielectric relaxation provide any insight into the nature of the excess wing in glycerol? To buttress our findings concerning the last question, we also present new high pressure dielectric results for another polyhydroxy alcohol, xylitol.

II. EXPERIMENT

The xylitol was obtained from Aldrich and used as received. For ambient pressure measurements, we used a Novo-Control GmbH Alpha dielectric spectrometer. The sample was contained in a parallel plate cell (diameter 10 mm, gap 0.1 mm). Temperature was controlled using a nitrogen-gas cryostat, with temperature stability better than 0.1 K.
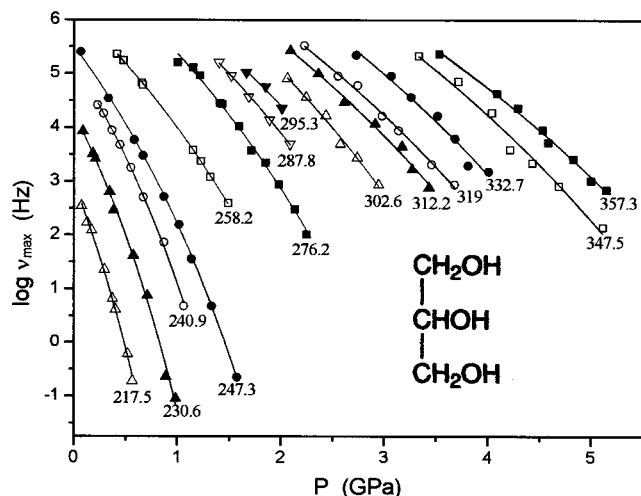

FIG. 1. Frequency of the maximum in the dielectric loss for glycerol at the indicated temperatures in degrees Kelvin. The chemical structure is shown. Data from Johari and Whalley (Ref. 9).

High pressure measurements employed the equipment described in Ref. 16. The sample was contained between two plates, and placed in the high-pressure chamber. Pressure was exerted via silicone fluid, using a chamber with a piston in contact with a hydraulic press. The pressure was measured by a Nova Swiss tensometric pressure meter (resolution = 0.1 MPa). The temperature was controlled within 0.1 K by means of a thermostatic bath.

III. RESULTS

A. Fragility

In Fig. 1 are shown the frequency of the peak maxima of the dielectric loss ($\nu_{max} = 1/2\pi\tau_\alpha$) reported by Johari and Whalley,[9] for glycerol at various pressures. The curves are the best fits to Eq. (2), using a common value of $D_p (= -11.0 \pm 1.1)$ for all temperatures. While this pressure equivalent of the VFTH equation describes the results well, there is insufficient structure in these data to choose among various models for the effect of pressure on τ. For example, we find that the expression of Casalini et al.,[17] derived from the Adam–Gibbs model,[18] works equally well: Such fits are indistinguishable from those using Eq. (2), and hence they are not shown herein. Thus, our use of Eq. (2) for interpolation is not meant to suggest its superiority over other approaches.

From the data in Fig. 1, we can calculate the activation volume using Eq. (5). Since ΔV is pressure dependent, we calculate the value at a pressure, P_g, for which $\tau = 100$ s. For temperatures above 250 K, this requires a substantial extrapolation of the measured data. The results are shown in Fig. 2, with the values for P_g displayed in Fig. 3. Since the condition of both temperature and pressure define a glass transition (at which $\tau = 100$ s), we can identify the former with the glass temperature associated with the corresponding pressure.

Included in Fig. 3 is the $T_g (= 189$ K) determined from ambient pressure measurements.[19,20] The dependence of T_g on pressure is nonlinear, consistent both with viscosity mea-
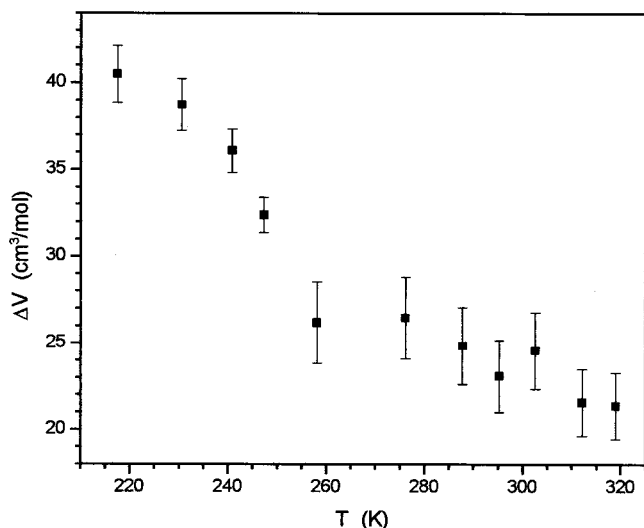
FIG. 2. Activation volume for glycerol at a pressure for which $\tau = 100$ s, calculated from the data in Fig. 1 using Eq. (5).

FIG. 4. The steepness index, calculated using Eq. (6), as a function of pressure for glycerol. After an initial increase, the fragility becomes independent of pressure for $P > 1$ GPa.

surements on glycerol[13] and the predictions of a lattice model.[21] From the initial slope, we obtain 35 K/GPa for the pressure coefficient of the glass temperature. This is close to the value of $dT_g/dP = 40$ K/GPa obtained by thermal analysis.[22] The pressure dependence of glycerol's T_g is insensitive to pressure, in comparison to other glass formers, for which values as high as 260 K/GPa have been reported.[23]

These data can be fit using the empirical equation of Andersson and Andersson,[24]

$$T_g = a\left(1 + \frac{b}{c}P\right)^{1/b}. \tag{7}$$

Given the required extrapolation to $\tau = 100$ s, our analysis is less reliable for higher pressures. Accordingly, we limit the
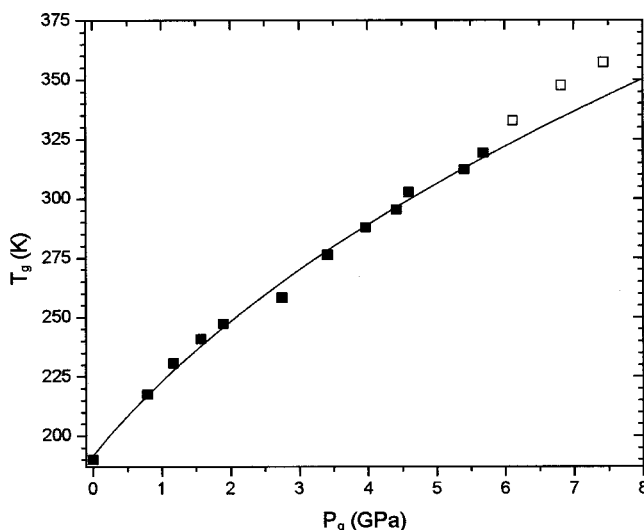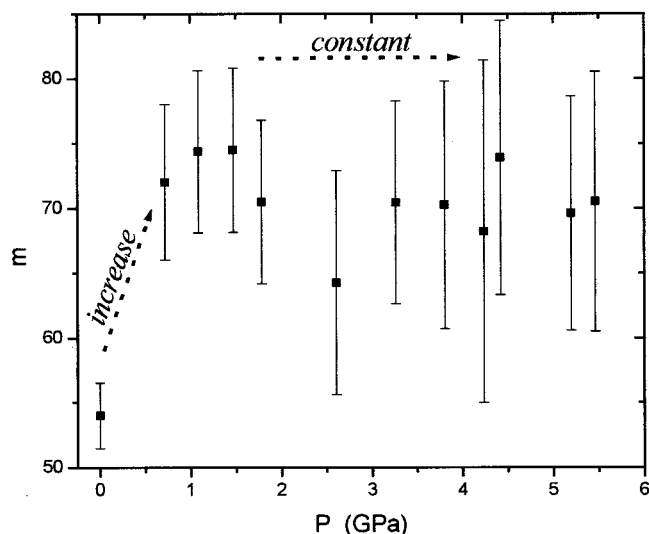

FIG. 3. Temperature dependence of the pressure at which the relaxation time equals 100 s, determined from the fit of Eq. (2) to the data in Fig. 1. The solid line through the data represents the fit of Eq. (7) to the data below 6 GPa (closed symbols). The initial slope yields 35 K/GPa for the pressure coefficient of the glass temperature.

fit of Eq. (7) to pressures below 6 GPa. Over this range, the data are well described using $a = 191.84$ K, $b = 2.637$, and $c = 5.420$ GPa, as shown in Fig. 3.

From Eqs. (6) and (7), we calculate the fragility

$$m = \frac{c\Delta V}{\ln 10Ra\left(1 + \frac{b}{c}P\right)^{(1/c)-1}} \tag{8}$$

with the results shown in Fig. 4. Also included is a single datum, $m = 54$, for ambient pressure, calculated from literature data.[19,25,26] The fragility is seen to initially increase with pressure, before becoming constant for P greater than ~ 1 GPa. This behavior is quite different from that reported by Cook et al.[13] from viscosity measurements on glycerol.

To demonstrate that the present results are not an artifact of the extrapolation of the data in Fig. 1, we recalculate the steepness index using $\tau(T_g) = 1$ s. This gives values of m roughly 10% lower than the calculated using $\tau(T_g) = 100$ s; however, the pattern in Fig. 4 is unchanged.

B. Relaxation function

There is a well-established correlation between fragility and the breadth of the α-relaxation function. Accordingly, the results in Fig. 4 suggest that the dispersion in the dielectric loss for glycerol will initially broaden under application of pressure, and then become invariant to further increases in pressure. In Fig. 5 we show the dielectric loss peak for glycerol at ambient pressure[25] and at $P = 91$ MPa.[16] The respective temperatures for these spectra (234 and 245 K) were chosen such that the frequencies of their dielectric loss maxima ($\nu_{max} \sim 10^5$ Hz) coincide, after a shift of less than 0.4 decades. As can be seen in Fig. 5, the peaks have identical shapes.

Spectra for lower temperatures [$\nu_{max} \sim 10$ Hz, which is closer to the assumed condition for the glass transition of
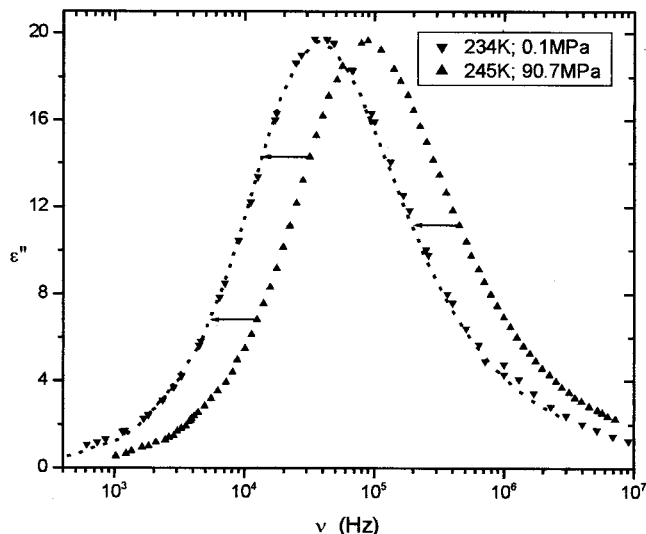
FIG. 5. α dispersion in the dielectric loss for glycerol at 234 K and ambient pressure ($\blacktriangledown$) and at 245 K and $P = 91$ MPa ($\blacktriangle$). These temperatures were chosen such that the respective ν_{max} were nearly equal. Shifting in frequency by a factor of 0.43 superposes the peaks.

$\tau_\alpha(T_g, P_g) = 100$ s] are shown in Fig. 6. It is common to represent the frequency dependence of the α relaxation using the Cole–Davidson function[27]

$$\epsilon''_{CD}(\nu)$$

$$= \Delta \epsilon \cos(\arctan(2\pi\nu\tau_{CD}))^\beta \sin(\beta \arctan(2\pi\nu\tau_{CD}))$$

$$(9)$$

in which $\Delta\epsilon$ is the relaxation strength, β the shape parameter, and τ_{CD} the relaxation time ($\tau_\alpha \sim \beta \times \tau_{CD}$). From the fits of the spectra (Fig. 6) to Eq. (9), it can be seen that the peak is broader on the high frequency side at elevated pressure (β
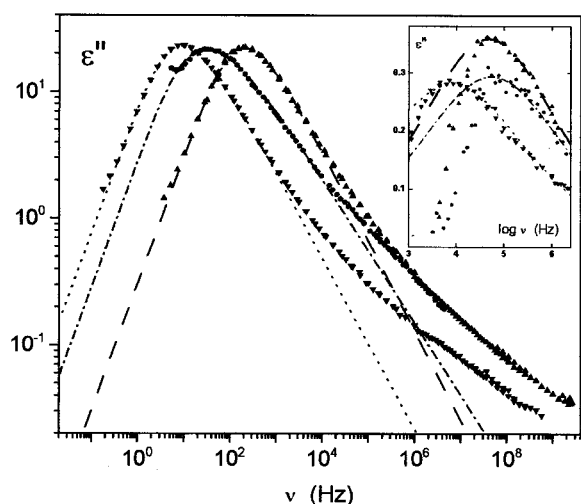

FIG. 6. α dispersion in the dielectric loss for glycerol at atmospheric pressure (204 K $\blacktriangledown$; 213 K $\blacktriangle$)—Ref. 25—and at $P = 91$ MPa (243 K; $\bullet$)—Ref. 14. The temperatures of the ambient pressure measurements were chosen to bracket the peak obtained at elevated pressure. The dashed lines indicate the contribution of the primary α relaxation estimated using Eq. (9). The inset shows the spectra after subtraction of the respective fits to the Cole–Davidson function, with the dashed lines representing the best fits to Eq. (10).
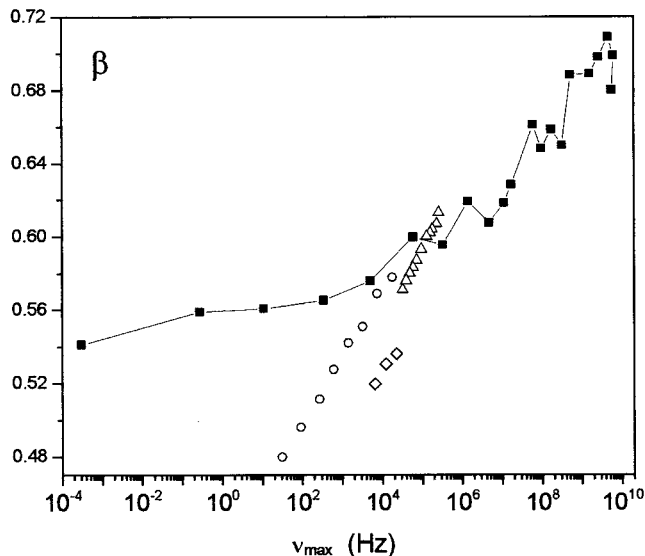

FIG. 7. The exponent of the power law describing the high frequency flank of the α relaxation, for glycerol at atmospheric pressure and $184 \text{ K} \leqslant T \leqslant 413$ K ($\blacksquare$)—Ref. 25—and at elevated pressure: 243 K ($\bigcirc$) and 258 K ($\Diamond$) for $P \leqslant 1$ GPa (Ref. 14); 245 K for $P < 0.3$ GPa ($\triangle$)—Ref. 16.

$= 0.48$ at $P = 91$ MPa) than at ambient pressure ($\beta = 0.56$). Thus, closer to the glass temperature, the peak shape becomes pressure dependent, which is consistent with the initial increase of fragility with pressure seen in Fig. 4. That is, the correlation of fragility with peak breadth is maintained, at least over the range $0 < P < 1$ GPa.

We summarize these results in Fig. 7 by plotting, for measurements made at both ambient[25] and elevated pressure,[14,16] the Cole–Davidson shape parameter (which is the exponent of the power law describing the high frequency flank of the α relaxation) as a function of ν_{max}. For $\nu_{max} < 10^4$ Hz, there is a marked broadening of the peak (smaller β) in going from ambient to elevated pressure ($P < 1$ GPa), consistent with the increased fragility over this range of pressures (Fig. 4).

C. Excess wing

Evident in the spectra in Fig. 6 is a departure from the power law associated with the high frequency side of the Kohlrausch-Williams-Watts (KWW) function. It is also apparent that under pressure, this high frequency wing in the spectrum becomes more prominent. We can examine this in more detail by subtracting the fitted KWW function from the measured data. The results are shown in the inset to Fig. 7, along with a fit of this excess intensity to the Cole–Cole function[28]

$$\epsilon''(\nu) = \Delta\epsilon_\beta \text{Im}\left[\frac{1}{1 + (i2\pi\nu\tau_{CC})^{1-\alpha_{CC}}}\right]$$

$$(10)$$

in which $\Delta\epsilon_\beta$ is the relaxation strength, τ_{CC} a relaxation time, and α_{CC} the shape parameter. These fits serve only as a visual guide; obviously, the data on the low frequency side of the peak maxima, representing a small difference between two large numbers, are subject to large error.

It can be observed that, while the primary peak measured under high pressure falls at lower frequency than the peak for
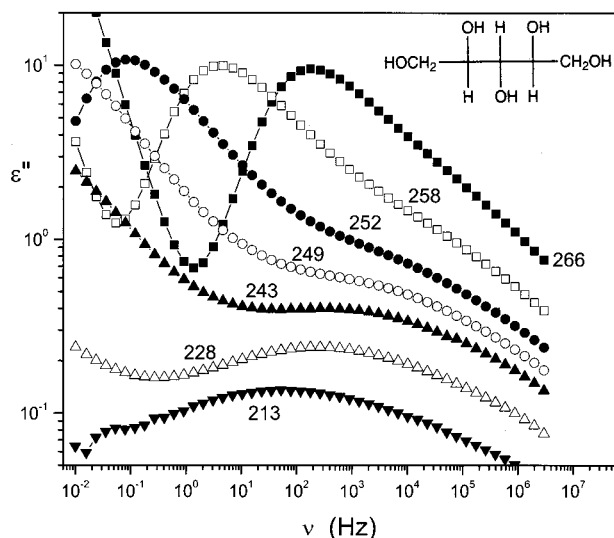
FIG. 8. Dielectric loss spectra for xylitol (chemical structure as shown) at atmospheric pressure and the indicated temperatures in degrees Kelvin (Ref. 29). An apparent excess wing observed at 258 K evolves into a distinct relaxation peak at lower temperatures.
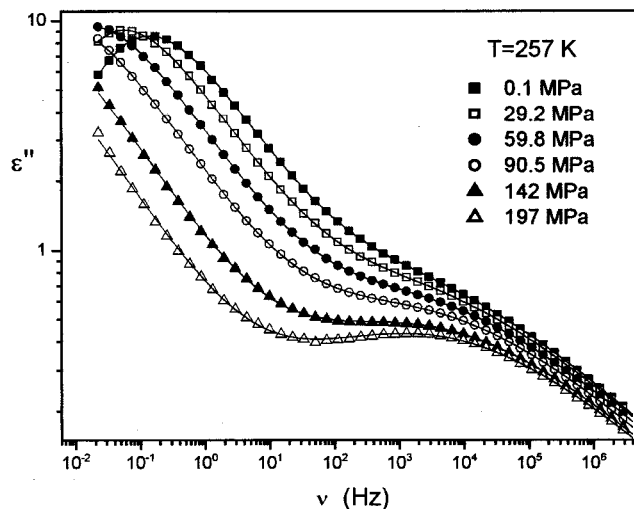

FIG. 9. Dielectric loss spectra for xylitol at the indicated temperature and pressures. The secondary relaxation becomes more prominent with increasing hydrostatic pressure.

213 K and ambient pressure, the corresponding residual peaks are at the same frequency. That is, the separation between the primary α relaxation and the high frequency peak increases with pressure. This gives rise to the greater prominence of the excess wing in the spectrum for $P=91$ MPa in Fig. 6.

D. Xylitol

It is of interest to see whether the absence of any correlation with glycerol between the primary structural relaxation and the excess wing is observed in other glass formers. Toward this end, we extend recent results on the dielectric loss of xylitol[29] with measurements at elevated pressures. Xylitol is a polyhydroxy alcohol similar to glycerol (cf. structures in Figs. 1 and 8).

In Fig. 8 are the spectra measured at ambient pressure.[29] At the higher temperatures, the dielectric loss peak is reminiscent of glycerol's—there is a change in slope at high frequencies, with the appearance of a putative excess wing. However, unlike glycerol, at lower temperatures (below $\sim$250 K) xylitol exhibits a distinct secondary peak. It is the overlapping of this peak with the primary α relaxation that gives rise to the extra wing intensity at higher temperatures.

In Fig. 9 we display dielectric loss spectra of xylitol measured for various pressures. Similar to glycerol, the temporal separation between the primary α relaxation and the high frequency wing increases with increasing hydrostatic pressure. (Although the effect of pressure on the α-relaxation times is much greater for xylitol than for glycerol.) As a result, the apparent excess wing at higher temperatures and ambient pressure (Fig. 8) is clearly resolved into a secondary peak upon application of high pressure.

The α-relaxation spectra for xylitol at ambient pressure and at $P=0.19$ GPa are shown in Fig. 10, for respective temperatures (262 and 272 K) such that the peak maxima coincide. The excess intensity at high frequencies becomes

more prominent for high pressure, qualitatively the same behavior as observed for glycerol (cf. Fig. 6).

IV. DISCUSSION AND SUMMARY

Previously it was reported that the fragility of glycerol,[13] as deduced from its viscosity, increases with pressure up to 3 GPa. However, we find herein that after an initial increase, beyond about 1 GPa, the fragility extracted from dielectric data is invariant to pressure. The dependence of the shape of the relaxation function on pressure is more complicated. At lower temperatures, approaching T_g, the spectra under elevated pressure are broader than for ambient pressure. This suggests that the correlation between fragility and peak shape holds for glycerol. However, whether the breadth of
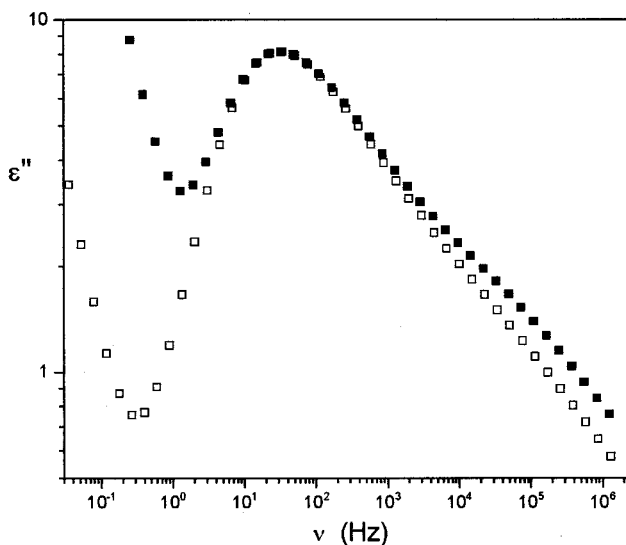

FIG. 10. Dielectric loss spectra for xylitol at atmospheric pressure (262 K; □) and at $P=0.19$ GPa (272 K; ■). The structural relaxation times under these conditions are essentially equal. Note that the excess wing responds differently to pressure than does the primary peak.

the structural relaxation function becomes invariant to pressure at higher pressures, in the manner of the fragility (Fig. 4), requires more data than is currently available.

The α-relaxation peaks for both glycerol and xylitol show an excess intensity at higher frequencies. However, these glass formers are categorically different (classifiable as "type A" and "type B" systems, respectively[30]). At temperatures nearer T_g, xylitol exhibits a distinct secondary relaxation (Fig. 8), whereas this is never observed in glycerol. This absence for the latter leads to the different interpretations of its excess wing—an inherent part of the structural relaxation[19,31] or an unresolved Johari–Goldstein secondary relaxation.[32]

The use of hydrostatic pressure as an experimental variable elucidates this issue. As seen in Fig. 6, under elevated pressure the excess wing for glycerol is more separated from the peak maximum. This indicates that the properties of the primary and excess intensities are not correlated, consistent with the latter being an unresolved secondary process.[32] As shown in Fig. 10, xylitol at higher temperatures exhibits very similar behavior. However, data for xylitol at lower temperatures (Fig. 8) makes clear that its excess intensity is unambiguously the contribution from a secondary process. Accordingly, the results for xylitol corroborate an interpretation of the excess wing in glycerol as being a distinct relaxation process.

The use of pressure to resolve these overlapping peaks relies on a difference in the pressure coefficient of the respective relaxation times. Even for glycerol, which has a very low dT_g/dP coefficient (35 K/GPa from Fig. 3), pressure has a weaker effect on the secondary relaxation time than on τ_α. This can be rationalized from the idea that the secondary (Johari–Goldstein) process is relatively noncooperative.[33] The strongly intermolecularly correlated structural relaxation, being governed by "crowding couplings,"[34] is expected to be more sensitive to compression; consequently, pressure effects greater temporal resolution of the two processes.

We should point out that pressure does not always affect structural relaxation in the manner seen herein. For cresolphthalein-dimethylether[35] and phenolphthalein-dimethylether,[36] both "type B" glass formers, the dielectric α-relaxation peaks for isothermal and isobaric measurements superimpose when compared at equivalent values of the relaxation time; that is, at constant τ_α, there is no difference in peak shape due to pressure. The fragilities of these liquids are greater than those of glycerol and xylitol,[4] but it is unclear whether this underlies the differing behaviors. Certainly more work is required.

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