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Effect of large hydrostatic pressure on the dielectric loss spectrum of type-*A* glass formers

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New dielectric spectroscopy results are reported for propylene carbonate (PC), glycerol, and threitol, measured at very high (1.8 GPa) pressure. These glass formers all exhibit an excess wing in their dielectric spectrum above T_g. We show that the shape of the α peak and excess wing of PC are invariant to pressure and temperature, when compared at a fixed value of the α-relaxation time. However, for the hydrogen-bonded liquids, there is a marked breakdown of this temperature-pressure superpositioning, due to a change in chemical structure (i.e., concentration of hydrogen bonds) with change of temperature or pressure. For all these materials, we can conclude that the excess wing is merely a secondary relaxation, masked under ordinary conditions by the intense, overlapping α peak.

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The dynamics of supercooled liquids has attracted much recent attention, in particular concerning the role of secondary processes, such as the β relaxation and the excess wing, in the vitrification process. Although polar pendant groups, as commonly found in polymers, can give rise to secondary peaks in the dielectric spectrum [1], the pioneering work of Johari and Goldstein (JG) [2] showed that the β relaxation exists in rigid molecules, which lack intramolecular degrees of freedom. This indicates that the phenomenon is a general feature of the deeply supercooled and glassy state. In identifying the JG process and understanding its role in the glass transition, an added complexity is that its existence is problematic in some glass formers. The latter liquids lack a distinct secondary peak in their dielectric loss spectrum, instead exhibiting an extra intensity ("excess wing") on the high frequency side of the structural relaxation peak [3–5]. The excess wing is characterized by a slope having a smaller exponent than that of the high frequency flank of the α-relaxation peak. The nature and origin of the excess wing is in dispute. Early approaches treated it as an inherent part of the α relaxation [6], based on putative scaling arguments, with support from theoretical models [7]. Kudlik and coauthors [3] suggest that supercooled liquids relax according to either an excess wing or the β-relaxation mechanism. This leads to the classification of glass formers into type A, which have an excess wing but no secondary peak, or type B, which exhibit a β relaxation.

Recent experimental results have cast doubts on the validity of this classification scheme. Schneider and co-workers [8] reasoned that if the excess wing is actually a submerged β peak, separation from the α peak should be achieved after physical aging, since below T_g the α and the β relaxations have different aging dependences. It was found that indeed, for two well-known "type A" glass formers, glycerol and propylene carbonate, a shoulder, or nascent peak, developed in the vicinity of the excess wing after extended (>1 month) physical aging. Similar experiments on propylene glycol (PG) and salol gave equivalent results [9]. Dielectric spectra have also been obtained on the dimer and trimer of PG under elevated hydrostatic pressure [10,11]. Although these liquids have a non-JG secondary relaxation peak observable even at low pressure, under high pressure an excess wing becomes newly evident in the spectra. Moreover, for the PG trimer, this excess wing assumes the form of a distinct peak after aging at high pressure [11]. The excess wing can also be transformed into a shoulder by distributing the glass former in a second material having a higher T_g. The latter preferentially slows down the α relaxation, to better isolate the secondary peak. This has been demonstrated for PC mixed with poly(methyl methacrylate) gels [12]. Thus aging, high pressure, and blending experiments all indicate that the excess wing is a secondary relaxation, which ordinarily is too close in frequency to the α process to be discerned as a separate peak.

A prediction concerning the JG relaxation time τ_{JG} comes from the coupling model (CM) of Ngai, according to which [13,14]

$$\tau_{\mathrm{JG}} = (t_c)^{1-\beta_{\mathrm{KWW}}} \tau_{\alpha}^{\beta_{\mathrm{KWW}}}, \tag{1}$$

where τ_α is the α-relaxation time, β_{KWW} is the Kohlrausch-William-Watts (KWW) stretch exponent describing the shape of the α-relaxation function [15], and t_c is a temperature- and pressure-independent crossover time equal to about 2×10^{-12} s. Equation (1) has been shown to be reasonably accurate for various glass formers [10,16,17]. This CM analysis is of special interest when calculating τ_{JG} for the type A liquids, for which τ_{JG} turns out to be only slightly smaller than τ_α [18]. This result supports the notion that the excess wing is a JG relaxation, not observed as a peak due to overlap of the close lying α peak.

However, there are conflicting experimental results concerning the excess wing behavior. In earlier work, we have compared the variation with temperature and pressure of the α relaxation and the excess wing [19,20]. When compared at temperatures and pressures (near T_g) for which the α-relaxation time is constant, for van der Waals liquids, the shape of both the α peak and the excess wing were unchanged; that is, for constant τ_α, temperature-pressure super-

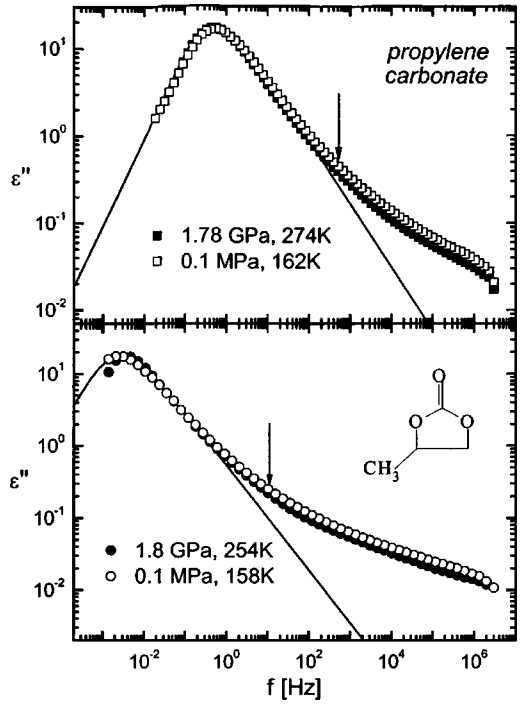

FIG. 1. Dielectric loss spectra of PC (chemical structure indicated) at ambient (open symbols) and elevated (filled symbols) pressure. The line is the best-fit to the KWW function. The arrow denotes the frequency of the JG relaxation calculated from Eq. (1).

positioning attains. This is not the case for H-bonded liquids, for which the α peak and the excess wing have somewhat different temperature and pressure dependences [20].

With these results in mind, it is of interest to compare the variation with pressure and temperature of the dielectric spectra of propylene carbonate and glycerol, two prototypical type-A glass formers. In these experiments, we compare spectra at different temperature and pressures, while maintaining constant the α-relaxation time. We do this near T_g in the equilibrium liquids; the excess wing becomes more apparent as the glass transition is approached by reduction in T or increase in P. To observe significant effects, the applied pressure has to be adequate to cause substantial changes in density. This makes glycerol an inconvenient liquid for pressure studies, given its rather small pressure sensitivity; the coefficient $dT_g/dp = 35$ K/GPa [21]. Accordingly, we utilize a pressure chamber allowing pressures as high as 1.8 GPa, whereby changes of the dielectric properties can be observed even in glycerol. In addition to the data for PC and glycerol, we also present herein interesting results for threitol, which has an excess wing that becomes a peak at sufficiently low temperatures [22]. The results of the present study make it clear that glycerol and PC cannot be considered as representatives of the same group, notwithstanding their common designation as type-A glass formers.

In Figs. 1 and 2(a) we show the respective spectra of PC and glycerol (the chemical formulas are included in the figure), measured at ambient and elevated pressures. To emphasize the interesting result for PC, we show spectra obtained for two different combinations of temperature and high pressure. The excess loss toward high frequency is apparent in these spectra as a deviation from the fitted KWW function.

Comparing the results, it can be observed that the excess wing behaviors are diametrically opposite. For PC, over the entire frequency range, the spectra superpose to within the experimental accuracy; however, for glycerol, there is a marked change in shape of both the primary peak and the wing. This result is consistent with previous work, in which type-A glass formers exhibit a distinctly different response to pressure, depending on whether they are van der Waals (e.g., phenylphthalein-dimethylether [19], cresolphthalein-dimethylether [19], polychorinated biphenyls [23], 1,1′-bis (*p*-methoxymethylphenyl) cyclohexane [20], and PC) or associated (e.g., salol [20] and glycerol) liquids.

Although hydrostatic pressure does not change the shape of the excess wing in PC relative to that of the α-relaxation

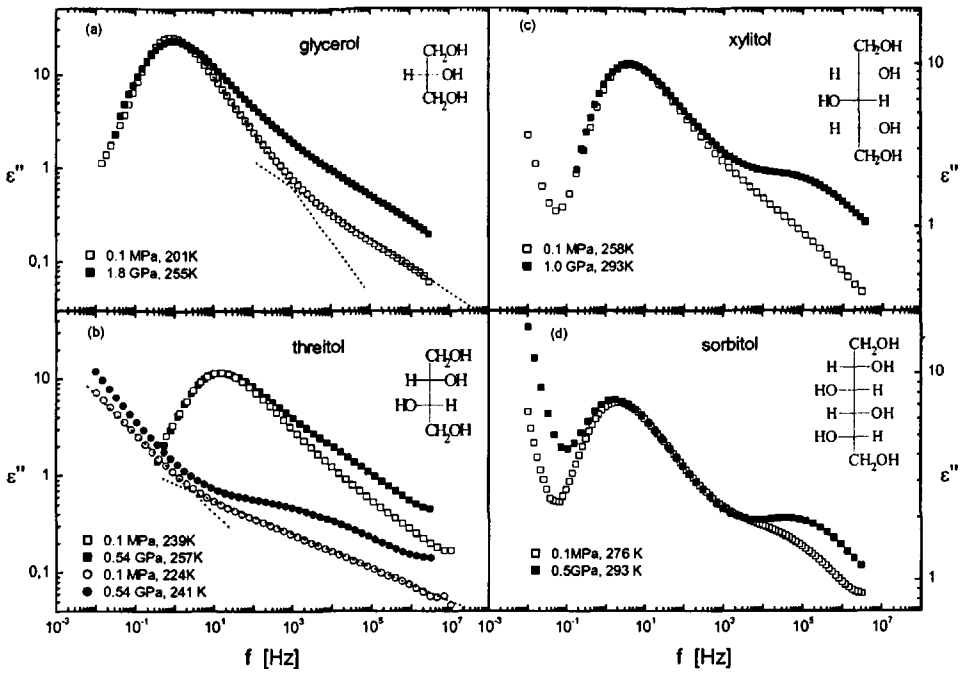

FIG. 2. Dielectric loss spectra of (a) glycerol, (b) threitol, (c) xylitol, and (d) sorbitol obtained at ambient (open symbols) and elevated (filled symbols) pressures. The chemical formulas are as indicated. The dashed lines in (a) represent the power law behavior on the high frequency side of the α relaxation, characteristic of the KWW function.

peak, this does not mean it is not a submerged JG process. Indeed, given the intermolecular character of a JG relaxation, a substantial pressure dependence is expected [10]. In combination with the fact that the shape of the α peak is constant for fixed τ_α, the superpositioning is expected [viz., Eq. (1)]. From the value of $\beta_{KWW}=0.73$ obtained from fitting the α peak in Fig. 1, we use Eq. (1) to calculate the expected frequency of the JG peak in PC. This characteristic frequency, denoted by the arrows in the figure, falls in proximity to the broad excess wing. These results are consistent with previous studies suggesting that excess wing in PC is a JG relaxation [8,12].

Since the breakdown of temperature-pressure superpositioning in glycerol is ascribed to the presence of hydrogen bonds, it is of interest to compare its behavior to other polyalcohols. Glycerol has three carbon atoms, while threitol, xylitol, and sorbitol have respectively four, five, and six carbons in the molecule. In Fig. 2 we show the chemical formulas for all four liquids. Xylitol and sorbitol are well known "type-B" glass formers [22], exhibiting distinct JG-relaxation peaks, as can be seen in their dielectric spectra in Fig. 2. The spectrum of threitol has the appearance of an excess wing at high temperatures, but well below T_g, a secondary peak emerges [22]. Thus, in the equilibrium liquid, threitol and glycerol appear very similar. However, in the glassy state, a JG relaxation for glycerol is only seen after extended physical aging [8]. For both liquids, the excess wing responds differently to pressure than does the α peak, causing the changes in shape of the spectra as seen in Figs. 2(a) and 2(b). Clearly, glycerol should be considered as a type-B glass former, in which the excess wing is only due to the overlapping α peak. The same conclusion was also reached by Nozaki [24] from extrapolating the behavior of sorbitol-xylitol mixtures. In fact, an analogous conclusion can be also inferred from recent NMR studies of Rössler and co-workers [25]. Direct observation of the JG peak in glycerol, however, unlike conventional type-B glass formers, requires large hydrostatic pressures [Fig. 2(a)] or extended physical aging [8].

Clearly, the results presented herein call into question the very designation of liquids as type A or B. It is striking that liquids, which conform to T-P superpositioning, have a relatively large sensitivity to pressure (for PC, $dT_g/dp \geqslant 70$ K/GPa [26]), in comparison to sorbitol (40 K/GPa [16]) or glycerol ($dT_g/dp=35$ K/GPa [21]), for which superpositioning fails. This, of course, reflects the fact that H-bonded liquids have small pressure coefficients [27]. The mechanism underlying this behavior is the effect temperature and pressure have on the concentration of hydrogen bonds. Approaching T_g from the equilibrium state by supercooling *increases* the number of H bonds, whereas if pressure has any effect, it likely reduces the degree of hydrogen bonding [20,28,29]. Moreover, since high pressure measurements are usually carried out at higher temperatures (to maintain τ_α constant), the effect is invariably a decrease in hydrogen bonding for higher pressure. Thus herein, with increasing carbons, the strength of the H bonding decreases, as reflected in greater separation of the α and JG peaks (Fig. 2). Unlike strictly van der Waals glass formers such as PC, the chemical structure of the polyalcohols changes with pressure, giving rise to a breakdown of superpositioning of the α and JG peaks in the dielectric loss.

To summarize, the excess wing in both glycerol and threitol is shown by high pressure measurements to simply be the high frequency flank of the secondary relaxation. While this statement also pertains to PC, the pressure invariance of the chemical structure of nonassociated type-A glass formers precludes separation via pressure of the excess wing to form a distinct peak.

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