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Letter

Generic α relaxation in a strong GeO_2 glass melt

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The viscoelastic α relaxation in glass-forming GeO_2 was measured over a range of temperatures near the glass transition using photon correlation spectroscopy. The relaxation in this "strong" glass former exhibits a nonexponential decay identical to that found in a great many simple organic "fragile" liquids. This finding contradicts the longstanding conjecture that nonexponentiality of viscous relaxations near the glass transition are correlated to the liquid's fragility. Instead, the findings offer support for a recent proposal that the nonexponentiality parameter of the α-relaxation in supercooled liquids displays a universal value $\beta(T_g) = 1/2$ near the glass transition.

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A striking feature of glassy materials is the complexity of the viscous dynamics [1–4] these supercooled liquids display near the conventional glass transition (T_g) where the viscosity reaches some 10^{12} Pa and the timescale for molecular reorientations begins to exceed 1 min. Just above T_g, the primary viscous relaxation (the α-relaxation), measured by techniques like dielectric spectroscopy and dynamic light scattering, generally exhibits a nonexponential decay in time that is often well described by a stretched exponential:

$$\phi(t) = \exp\{-(t/\tau)^{\beta}\}. \tag{1}$$

For many simple molecular liquids [5,6], the stretching exponent, β, ranges from 0.3 to 0.7, and the average relaxation time, defined by $\tau_{\text{avg}} = \tau\Gamma(1/\beta)/\beta$, where $\Gamma(x)$ is the usual gamma function, parallels the viscosity. In addition to the nonexponential decay, these same liquids generally exhibit a non-Arrhenius temperature dependence. Namely, in a plot of $\log \tau_{\text{avg}}$ versus inverse temperature, the data display substantial curvature with a low slope at high temperatures and a high slope at lower temperatures. In fact, the magnitude of the deviation from Arrhenius is often characterized by a so-called fragility index [5],

$$m = d \log \tau_{\text{avg}}/d(T_g/T)|_{T_g}, \tag{2}$$

evaluated from the slope just near T_g . Values of the index range from a minimum of $m \approx 16$ for Arrhenius behavior to values in excess of $m = 100$ found in some polymeric liquids [5,6].

In a 1993 survey [5] of over 50 glass-forming materials, including organic liquids, polymers, and network-forming oxides, the values of β near T_g were compared with the fragility indices to suggest that a general correlation exists between the nonexponentiality of the relaxation and its non-Arrhenius temperature dependence. This survey has been cited more than 2500 times [7] in the intervening years, giving rise to a general perception in the field that the more fragile a melt is, the more nonexponential will be its decay process [5,8,9]. The correlation is strengthened considerably at the high-fragility end by the inclusion of many fragile polymer liquids such as polyvinylchloride ($m \approx 190$) and polystyrene ($m \approx 140$), with $\beta(T_g) \approx 0.24$ and 0.35, respectively. But, it is also strengthened at the opposite extreme by the inclusion of two "strong" ($m = 20$) network-forming oxides, SiO_2 and GeO_2, with $\beta(T_g)$ reported [10,11] to be 0.7 and 1.0, respectively.

A more recent survey [6] has, however, challenged this thinking. An extensive study of over 50 molecular liquids using broadband dielectric spectroscopy has revealed the prevalence of $\beta(T_g) \approx 1/2$ independent of fragility. Challenged by some [12,13], but supported by others [14–18], the finding suggests there may exist a generic α-relaxation that is universal among all glass-forming liquids sufficiently close to T_g (where the α-relaxation can be properly separated from other overlapping relaxation processes). Moreover, this specific stretching exponent can be easily interpreted within several simple theoretical models [19,20], leading to speculation that glassy dynamics might not be as complex as once thought.

A weakness of both surveys is their emphasis on molecular liquids at the near exclusion of "strong" oxide glass formers like SiO_2 and GeO_2, with a fragility ($m \approx 20$) that makes them nearly Arrhenius over the entire temperature range. Unlike molecular liquids with weak, isotropic bonding that promotes highly cooperative molecular reorientations involving many neighboring atoms, molecular rearrangement in the oxides occurs via the breaking and reformation of discrete, covalent bonds within a continuous random network [21]. Given these chemical and structural differences, one might anticipate corresponding differences in the dynamics, vis-à-vis the nonexponentiality.

In this Letter, we report an unprecedented dynamic light-scattering study of molten GeO_2 conducted at temperatures just above the glass transition. In difference to a half-century-old report [11] that the viscous relaxation in GeO_2 is exponential, we observe an α-relaxation that is considerably nonexponential. In fact, we find that $\beta(T_g)$ approaches a value

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of 1/2, identical to the universal value reported recently [6] in many simple molecular liquids. This suggests the universality observed in some organic liquids may be expanded to include covalently bonded liquids as well.

Germanium (IV) oxide (99.9999%, Alfa Aesar) was found to be sufficiently free of unwanted insoluble matter that reliable scattering from the liquid alone could be observed in a homodyne mode [22] of detection. The powder was loaded into a precleaned silica ampoule (6 mm i.d. × 8 mm o.d.) and melted following the procedure described by Nemilov [23]. The powder was first heated at 1000 °C for 2 h to remove any moisture and then melted at 1300 °C. After melting, the sample was degassed under vacuum (<200 mTorr) and then raised in temperature to 1520 °C for 2 h to allow the melt to settle into the bottom of the ampoule. This resulted in a colorless, transparent, and bubble-free melt. Once settled, the sample was stored at 1180 °C (just above the melting point) overnight before light scattering was performed.

The sample was quickly transferred to a preheated optical oven near 900 °C. The optical oven, described previously [24], maintains the sample at a fixed temperature stable to within ±0.1 °C and allows for laser light to be focused into the ampoule and scattered light to be collected. Approximately 800 mW of coherent light (532 nm) from a laser (Coherent, Verdi 5) was focused by a lens into the interior of the ampoule and the light scattered at 90° was first passed through a laser line filter (∼10-nm bandpass), then collected by a second lens and imaged onto a 50-µm pinhole located approximately 0.5 m in front of the photoactive region of a photomultiplier tube [(PMT) Thorn EMI 9863/350]. Photopulses generated by the PMT were converted to a digital (transistor-transistor logic) equivalent and input to an autocorrelator (correlator.com) that computed the autocorrelation of intensity fluctuations in the scattered light, $C(q,t)$, which is directly related [22] to the dynamic structure factor, $S(q,t)$:

$$C(q,t) = \frac{\langle I_q(t'+t)I_q(t')\rangle}{\langle I_q(t')^2\rangle} = 1 + A_{\mathrm{COH}}|S(q,t)|^2$$
$$= 1 + A_{\mathrm{COH}}\left|f_o \exp\{-(t/\tau)^{\beta}\}\right|^2. \quad (3)$$

Here, the coherence factor, $A_{\mathrm{COH}} = 0.82 \pm 0.02$, is an instrumental constant determined by the collection optics and calibrated using a suspension of scattering microspheres [24]. Autocorrelation functions were accumulated at a series of fixed temperatures above the glass transition temperature. Each was accumulated over a sampling time in excess of 1000 times the value of τ.

Examples of the autocorrelation obtained are shown in Fig. 1. The autocorrelations are well described by the stretched exponential form given in Eq. (3), and an example of the fitting residuals is included in the figure. Results of the curve fitting are summarized in Table I. We observe a nonergodic level, $f_o = 0.74 \pm 0.02$, that appears independent of temperature, and a decay that slows and stretches with decreasing temperature. The nonergodic level marks a plateau in $S(q,t)$, separating faster decay processes from the slower α-relaxation [1]. Our nonergodic level (here in the $q = 0$ limit) compares favorably with the values between 0.58 and 0.85 (mean of $f_q = 0.75$) reported in quasi-elastic neutron scattering [25] of GeO_2 over a range of scattering wavevectors $0.7 < q < 3.6$ Å^{-1}. Analysis of the temperature dependence of the average relaxation time in Fig. 2 indicates a highly Arrhenius form with an activation energy of 68 kcal/mol that is similar to, but slightly less than, the 72.6 ± 0.3 kcal/mol reported for the viscosity [11,23]. Extrapolation of the graph to $\tau_{\mathrm{avg}} = 100$ s provides a measure of $T_g = 585 \pm 5$ °C, which can be compared with values of $T_g = 565$ °C [23], 550 °C [11], 487 °C [26], and 476 °C [27] reported from calorimetric and viscosity measurements. Like many oxide glasses, the glass transition temperature of GeO_2 decreases sharply [21,26] with the addition of minor amounts of water or alkali oxides (even fewer than 0.01 mole%), and our result here suggests such impurities have been successfully mitigated. Upon rescaling the temperature axis of Fig. 2 to T_g, we determined the fragility to be $m = 16.7 \pm 0.2$, which is extremely non-

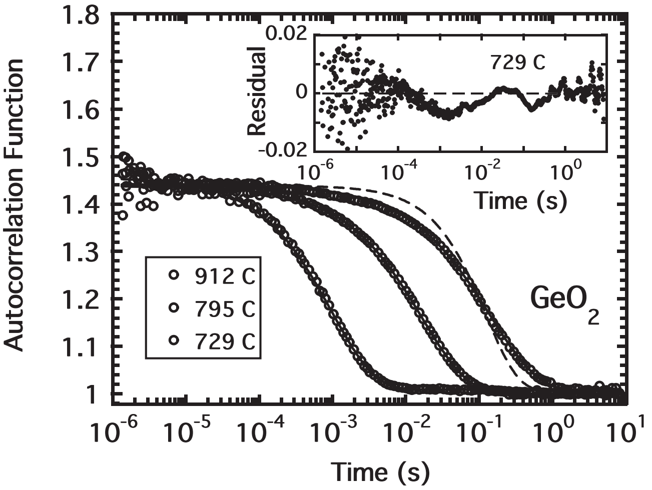

FIG. 1. Intensity autocorrelation functions obtained from GeO_2 at selected temperatures shown. Solid lines are fits to Eq. (3) and the dashed line is an exponential decay shown for comparison. (Inset) A plot of the curve fitted residuals for the autocorrelation collected at 729 °C shows deviations between data and fit are less than 1%.

TABLE I. Results of curve fitting of α-relaxation in GeO_2.

T (C)	τ (s)	β (±0.03)
923.7	0.00246	0.75
911.7	0.00257	0.72
894.4	0.00352	0.78
876.8	0.00493	0.76
859.0	0.00722	0.75
841.3	0.0116	0.73
823.3	0.0209	0.72
809.7	0.0261	0.71
794.5	0.0453	0.69
778.3	0.0913	0.66
760.3	0.142	0.66
744.2	0.203	0.66
728.8	0.416	0.64
713.2	0.611	0.61
692.4	1.25	0.58
678.3	1.68	0.54

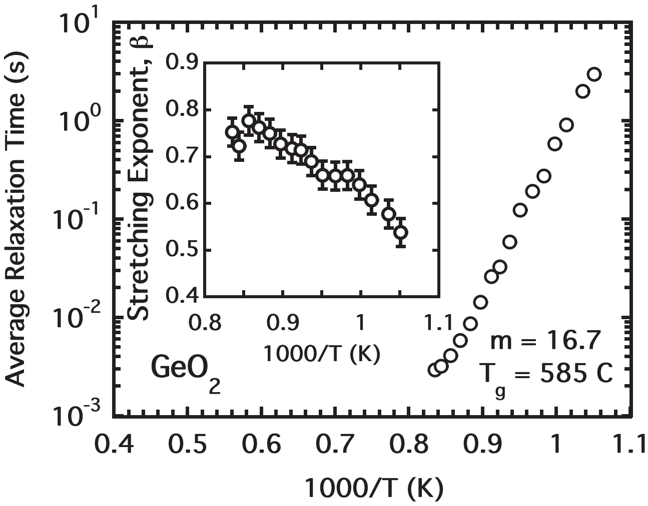

FIG. 2. The average relaxation time for the α-relaxation in GeO_2 as a function of inverse temperature. (Inset) The stretching exponent also as a function of inverse temperature.

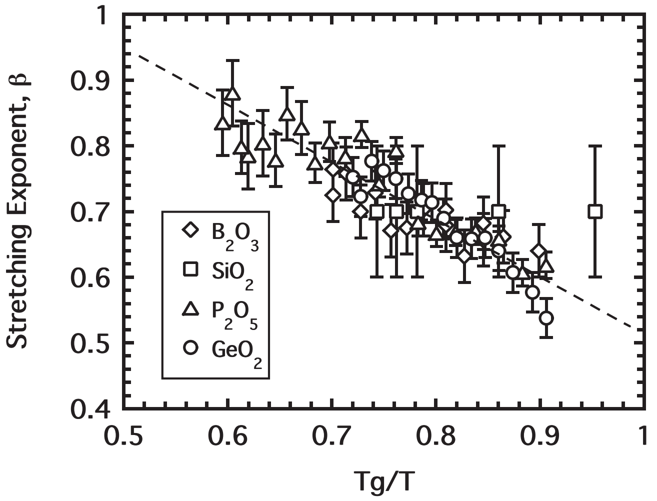

FIG. 3. Plot of the stretching exponents reported for four major oxide glasses [10,24,29] as a function of inverse temperature scaled to the individual glass transition temperatures. The dashed line is linear fit discussed in the text that extrapolates to $\beta(T_g) = 0.52$.

fragile. As shown in the inset to Fig. 2, the stretching exponent decreases steadily with decreasing temperature in a fashion that is not uncommon to some fragile glass-forming liquids [28]. The value of β appears to be approaching $\beta(T_g) \approx 1/2$ as the glass transition ($1000/T_g \approx 1.16$) is approached. At no temperatures in the current study do we observe a purely exponential relaxation, in contradiction with earlier reports [5,11]. This disagreement may might be attributed to the nonequilibrium character of the previous study [11], which concluded a Debye-like spectrum of relaxation times ($\beta = 1$) based on annealing studies of volume relaxation following temperature jumps conducted below T_g. In contrast, the present measurements are of the α-relaxation obtained at thermal equilibrium above T_g.

It is worth stressing that the similarity in $\beta(T_g)$ found for GeO_2 with that of a great many organic liquids is somewhat surprising given the vastly different bond configurations at play in these different liquids. In simple van der Waals liquids like ortho-terphenyl, salol, or glycerol, the cohesion arises from relatively weak forces that act isotropically between neighboring molecules. There, molecular rearrangements are highly cooperative in the sense that the displacement of any single molecule can depend on the collective motion of a great many others [2,4], even beyond the nearest neighbor sphere. Fluctuations of free volume and steric hinderances can also play a pivotal role in facilitating the rearrangements, and the presentation of a nonexponential decay is not altogether unexpected. This is sharply contrasted with the bonding in oxide glasses like GeO_2, where the structure is built up of germanium and oxygen atoms interconnected by a network of discrete, directional bonds—a covalently bonded network in which rigorous rules of local coordination must be obeyed [21]. Unlike the collective rearrangements occurring in van der Waals fluids, flow in these network-forming oxides involves the release of local stresses when a covalent bond is temporarily ruptured and then later repaired. The process involves only a limited number of discrete bonds, involves little or no manipulations of free volume, and is thus far less cooperative than that occurring in van der Waals fluids. Despite these important differences, which do clearly influence the degree of non-Arrhenius temperature dependence, it is remarkable how the nonexponentiality appears to display a common, universal shape near the glass transition point.

Further support for this universality is found in a comparison of GeO_2 with three other major oxide glass formers, all of which are slightly less Arrhenius. Shown in Fig. 3 are $\beta(T_g/T)$ for P_2O_5 ($m = 19$) [24], SiO_2 ($m = 20$) [10], and B_2O_3 ($m = 32$) [29] plotted together with GeO_2 ($m = 16.7$). Except for one outlier in SiO_2, the data again support a common pattern of $\beta(T)$ decreasing with decreasing temperature and approaching a limiting value near 1/2 at T_g. Collectively, the trend can be expressed as $\beta(T_g/T) = 1.38-0.86(T_g/T)$ with an acceptable goodness of fit, $\chi^2_{\text{red}} = 1.05$, and extrapolates to a value of $\beta(T_g) = 0.52 \pm 0.06$.

The increase in nonexponentiality on approach to T_g seen in Fig. 3 is not atypical in studies of molecular liquids, especially those employing broadband dielectric spectroscopy. However, in many photon correlation spectroscopy (PCS) studies [14,30,31], the shape of the α-relaxation is often temperature independent. In these instances, the relaxation exhibits so-called time-temperature superposition (TTS), wherein spectra at different temperatures can be scaled in a simple fashion to collapse to a common curve [14]. Differences like these between dielectric spectroscopy and light scattering have recently resulted in considerable debate [12,13,32]. Not only is the shape of the relaxation complicated by secondary relaxation processes present at frequencies above the α-relaxation, but dielectric spectroscopy is uniquely sensitive to cross terms of the dipole correlation function that produce in a Debye-like contribution in the dielectric loss at frequencies below where the α-relaxation appears in light scattering. Some have recently suggested [12,13] these cross correlations are an inherent feature of the structural relaxation reproduced in mechanical loss studies, while others [15,16] contend the Debye process is a separate contribution seen only in the dielectric loss, but absent from PCS (which probes only a self-correlation of fluctuations). Although this Debye process at low frequencies could give rise to temperature-dependent changes in the shape of the dielectric loss like that seen in Fig. 3, the absence of this process in PCS would seem to rule out cross correlations as a source for the absence of TTS in our present case. It appears, then, that the $\beta(T)$ we observe may be a feature unique to covalently bonded network-forming melts.

Our findings here are impactful in three distinct ways. First, our study addresses a major data gap in the field of supercooled liquid dynamics. Namely, the vast majority of studies of α-relaxation in supercooled liquids are performed on molecular glass formers at temperatures near or below ambient using broadband dielectric spectroscopy. Comparable studies of network-forming oxides are far fewer, in part because there are simply fewer such glass-forming examples compared with molecular liquids, but also because the temperatures required to study these oxide melts pose significant limitations for conventional dielectric spectroscopy. In fact, the present study of the viscous response in GeO_2 is the only one to appear in over 50 years since the volume annealing study [11] that had earlier concluded that strong glasses relax exponentially.

Second, our findings solidly refute the long-held position that nonexponentiality is correlated to fragility. Aside from polymers, this correlation had relied heavily on GeO_2 as something of a "smoking gun"—a lone *prima facie* example of a very strong glass former with a purely exponential relaxation. Here we now see that in GeO_2 and other strong glass formers, the relaxation near T_g is simply *not* exponential.

Third, the results may significantly expand the universality of the generic α-relaxation. Up to now, this universality had only been identified in molecular glass formers studied at temperatures near enough to T_g that contributions from secondary relaxations could be separated from the α-relaxation [14]. Our finding of $\beta(T_g) = 1/2$ in several binary oxide glasses suggests nonexponentiality is both independent of the fragility and also a universal feature of supercooled liquids with vastly differing bonding environments.

In summary, our dynamic light-scattering measurements presented here reveal that the α-relaxation in GeO_2 is, in fact, significantly nonexponential, in contradiction to the standard viewpoint that such strong glass-forming materials exhibit an exponential decay. Our measurements also represent an effort to address a data gap in the study of supercooled liquids wherein the vast majority of past research has focused mostly on highly fragile liquids with weak van der Waal interactions, while very little effort has been spent on covalently bonded oxide melts. Remarkably, we find that when both fragile and strong liquids are considered together, they share the same universal nonexponential decay near the glass transition.

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