Role of hydrogen bonds in the supercooled dynamics of glass-forming liquids at high pressures

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The effect of pressure on the dynamics of supercooled liquids shows a variety of remarkable similarities for different glass-forming systems. However, an important group of liquids, characterized by hydrogen-bond interactions, show some deviations from these general behaviors. To investigate this, we use broadband dielectric spectroscopy to study the temperature dependent dynamics of a supercooled hydrogen bonded oligomeric glycol and its non-hydrogen-bonded analog over a wide range of pressures. With the chosen model system, we are able to directly link the presence of hydrogen bonding to deviations from the general pattern of the pressure response of supercooled dynamics.

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A liquid cooled below its freezing point undergoes a dramatic increase in viscosity and structural relaxation time. This slowing down of the dynamics is the key element in vitrification, whose origin remains to be fully understood. Materials with a wide variety of chemical structures and physical properties form glasses. A number of general properties, encompassing most nonassociated liquids and polymers, have emerged: (i) The structural (or α) relaxation time τ collapses onto a master curve if plotted versus the product TV^{γ}, where T denotes temperature, V the specific volume, and γ is a material constant reflecting the contribution of volume to the dynamics,[1–4]

$$\tau = \mathfrak{I}(TV^{\gamma}). \tag{1}$$

where $\mathfrak{I}$ is a function. (ii) The shape of the α-relaxation response function is uniquely determined by its relaxation time τ,[5,6] which means that at fixed τ, the α dispersion is invariant to temperature and pressure. (iii) The temperature dependence of τ or the fragility, as characterized by the T_g-normalized Arrhenius slope, $m_P \equiv \partial \log(\tau)/\partial(T_g/T)|_{T_g}$, where T_g is the glass transition temperature,[7] generally decreases with increasing pressure.[8]

Normally, the change of τ with T is governed to comparable degrees by thermal energy and density.[4] However, a number of liquids show clear deviations from this behavior, with reduced volume effects and an increased influence of temperature. Examples of such liquids are glycerol,[9] sorbitol,[10] and water.[11] In addition, for water, the scaling of τ [Eq. (1)] fails[11] and for glycerol, the superpositioning exhibits substantial scatter.[12] Moreover, glycerol shows a fragility that increases with increasing pressure,[13] in contrast to the generally observed behavior. Common for liquids with such "anomalous" pressure behavior is that they are characterized by hydrogen bond interactions. The implication is that the observed deviations from the general patterns are due to the hydrogen bonded nature of the intermolecular interactions.

To test this hypothesis, we investigate the effect of hydrogen bonding on the pressure dependent dynamics using broadband dielectric spectroscopy.[14] The glass transition dynamics takes place over an extremely wide range of time scales, which makes broadband dielectric spectroscopy an ideal technique. Furthermore, this technique has the particular advantage of making measurements under elevated pressure relatively easy. We study a supercooled hydrogen bonded glass-forming liquid heptapropylene glycol (7PG), having a degree of polymerization $n=7$, and its non-hydrogen-bonded analog, heptapropylene glycol dimethyl ether (7PGDE). For the dimethyl ether, the terminal hydroxyl groups are exchanged for methoxy groups ($O\text{-}CH_3$) to create an analogous structure lacking hydrogen bonding. Dielectric measurements at elevated pressures were carried out using a Harwood Engineering pressure cell and a Novocontrol Alpha analyzer. The dielectric response was measured for both oligomer samples as a function of pressure and temperature. The observed peak (see Fig. 2) in the dielectric loss due to structural relaxation was fitted with a Havriliak-Negami expression,[14] from which the average structural relaxation time was obtained.

Both the glycols (with hydroxyl end groups) and the dimethyl ethers (with methoxy end groups) based on propylene glycol oligomers are good glass formers and their supercooled dynamics have been studied previously using different techniques.[11,15–18] In this work, we focus on a direct comparison between the corresponding glycol and dimethylether heptamer with regard to the effect that hydrogen bonding has on the general patterns of behavior observed for the pressure dependence of supercooled liquid dynamics.

We start by investigating the first generality (i), the TV^{γ} scaling [Eq. (1)]. To do this, we determine the specific volume V of 7PG for all measurement temperatures T and pressures P using the PVT results of Zoller and Walsh[19] and fit these to the Tait equation of state,

$$V(T,P) = (v_0 + v_1 T + v_2 T^2) \times [1 - 0.0894 \ln\{1 + P/(b_0 \exp[-b_1 T])\}]. \tag{2}$$

The obtained parameters are given in Table I. The measured τ for different pressures can now be plotted vs TV^{γ}, where γ is adjusted to give the best superpositioning of the data. The results for $\gamma=2.7$ are shown in Fig. 1 and it is evident that the relaxation time τ is not uniquely defined by this product

TABLE I. Results for uncapped and capped propylene glycol heptamers.

	v_0	v_1	v_2	b_0	b_1	T_g[a]	E_V/E_P[b]	γ
7PG	0.9770	7.04×10^{-4}	9.8×10^{-7}	190	5.93×10^{-3}	205.8 K	0.73±0.03	~2.8[c]
7PGDE	1.0282	7.75×10^{-4}	10.1×10^{-7}	160	6.15×10^{-3}	178.0 K	0.69±0.01	3.1

[a]Temperature at which τ=0.1 s.
[b]At T_g.
[c]Calculated from Eq. (3) (τ do not scale).

variable. Unlike the results for more than 50 van der Waals glass-forming materials,[4] the scaling fails for 7PG. Using published *PVT* data for 7PGDE,[19] we can examine how the removal of hydrogen bonding affects the scaling. The results are plotted in Fig. 1 and show that as the hydrogen bonding is removed by end capping, the data can be superimposed. A value of the scaling exponent γ=3.1 is obtained, which is at the low end of the range found for molecular glass formers.[4] This is expected since the intramolecular bonds of this oligomer are less sensitive to pressure,[20] leading to a weaker response to volume changes. Generally, small molecules have higher γ values than polymers.[4]

Removal of the H-bonding capacity of 7PG thus results in conformance to the scaling behavior of Eq. (1), whereas the thermal lability and pressure sensitivity of hydrogen bonds[21,22] cause the TV^γ scaling to fail. A similar breakdown of the scaling is found for water,[11] a strongly associated liquid with a high concentration of H bonds. Consistent with this interpretation, we find that if the hydrogen bond density of 7PG is reduced by increasing the oligomer chain length, the scaling holds, as found for polypropylene glycol with n=69 for which γ=2.5 (Ref. 23) and for a random copolymer of ethylene and propylene glycol with n=45 and γ=2.3.[11] If the scaling is related to the steepness of the intermolecular potential,[24] the breakdown for hydrogen bonded systems is a reflection of differences in the shape of the potential for the different H-bond concentrations prevailing at different temperatures and pressures.

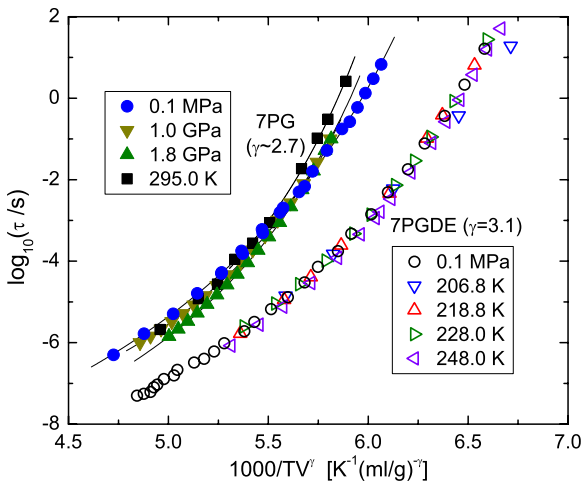

FIG. 1. (Color online) Failure of TV scaling due to hydrogen bonding. Structural relaxation times of hydroxyl terminated 7PG as a function of $TV^{2.7}$ and of 7PGDE as a function of $TV^{3.1}$. Since τ for the former do not superpose, the value of γ is arbitrary; Eq. (3) yields γ=2.8. The solid lines are from the reported Vogel-Fulcher fits of τ for the 7PG at ambient (Refs. 16 and 17) and elevated P (Ref. 16).

We next investigate the effect of hydrogen bonding on generality (ii), the invariance of the shape of the structural relaxation function for different combinations of temperatures and pressures when τ is constant.[5,6] For hydrogen bonded materials, this superpositioning of the structural α peak at fixed τ generally breaks down due to the change in hydrogen bond concentration,[5] and this is indeed the case for glycols. However, as shown in Fig. 2, the spectra measured for 7PGDE at various conditions of T and P, corresponding to fixed τ, superpose. The fact that for nonassociated liquids the shape (breadth) of the α peak depends only on the relaxation time means that the scaling exponent γ governs the shape of the α-relaxation dispersion, as well as the value of τ. Parenthetically, we note that upon application of pressure, for large τ an additional contribution appears on the high frequency flank of the α peak. Such a feature has been reported previously for 7PG in the glassy state at atmospheric pressure[17] and for lower molecular weight PG oligomers under high pressure[25–27] or mixed with water;[27,28] thus, certain conditions influence the H bonding, resulting in resolution of this spectral feature.

The effect of volume on the dynamics is reflected in the value of γ; however, a more common metric is the ratio of

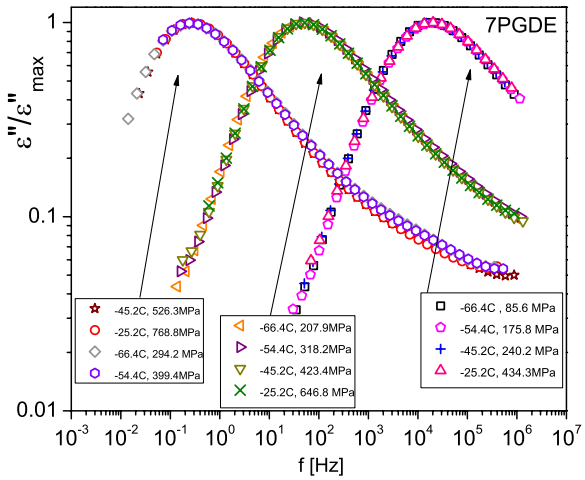

FIG. 2. (Color online) Invariance of the α dispersion peak shape at constant α peak frequency upon removal of the hydrogen bonding. Loss spectra of 7PGDE at various combinations of T and P (as indicated).

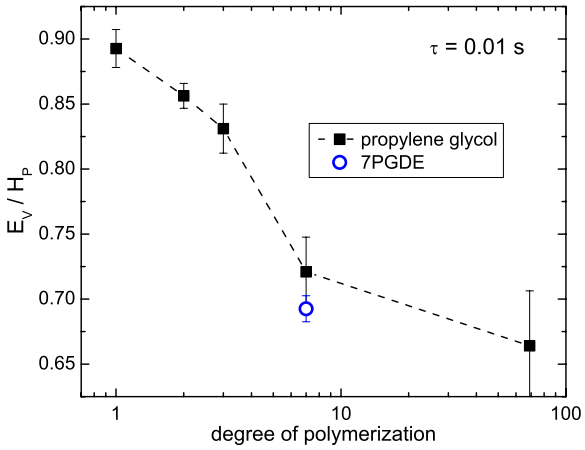

FIG. 3. (Color online) Decreasing the density of H bonding increases the influence of volume on the dynamics. Ratio of isochoric activation energy and isobaric activation enthalpy for propylene glycol having the indicated n; the open circle is the value for the 7PGDE. Data are from Ref. 30, except for the two heptamers.

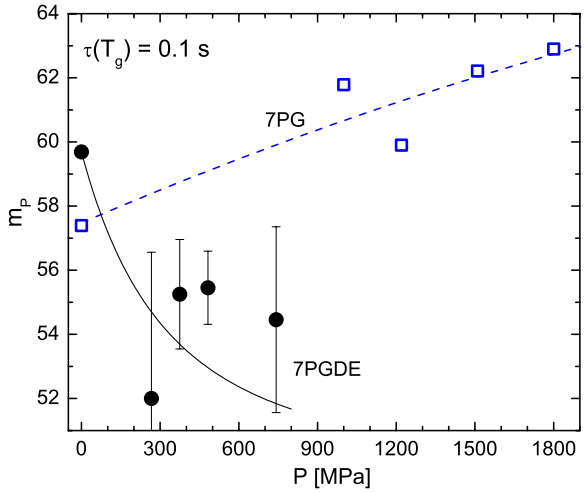

FIG. 4. (Color online) H bonding changes the sign of the P dependence of the fragility. Pressure dependence of the fragility for 7PG and 7PGDE, the former values calculated using the Vogel-Fulcher parameters in Ref. 16 (dashed line is only a guide for the eyes). For 7PGDE, m_P were calculated using both Eq. (5) (circles) and Eq. (6) (solid line).

the apparent activation energy at constant volume, $E_V(T,V) \equiv R\partial \ln \tau/\partial T^{-1}|_V$ to the activation enthalpy at constant pressure, $H_P(T,P) \equiv R(\partial \ln \tau/\partial T^{-1})|_P$.[29] This ratio, which varies from zero to unity with increasing relative influence of temperature, can be calculated from the scaling exponent,[4,8]

$$\frac{E_V}{H_P} = (1 + \gamma\alpha_P T)^{-1}, \tag{3}$$

where α_P is the isobaric thermal expansion coefficient. We will use this ratio to investigate the relative effect of volume on the dynamics for changes in H-bond density.

For the nonassociated oligomer, 7PGDE, we determine $E_V/H_P = 0.69 \pm 0.01$ for $T = 178.0$ K using a thermal expansion coefficient determined from the Tait parameters in Table I for $P = 0.1$ MPa and $\tau = 0.1$ s. The scaling exponent γ is independent of temperature and pressure, but as temperature is lowered or pressure increased, the ratio E_V/H_P increases, reflecting a weaker influence of volume.[20] Since the hydrogen bonded 7PG does not conform to the scaling of Eq. (1), we use the data of Ref. 16 to calculate the temperatures for which $\tau = 0.1$ s at various pressures. From the corresponding specific volumes, we calculate the isochronal thermal expansion coefficient, $\alpha_\tau = -1.65 \times 10^{-3}$ K^{-1} at 0.1 MPa and 205.8 K (a substantial extrapolation is necessary due to the gap between the published ambient and high pressure data.[16]) Using the relation[4]

$$\frac{E_V}{H_P} = (1 - \alpha_P/\alpha_\tau)^{-1}, \tag{4}$$

with $\alpha_P = 6.129 \times 10^{-4}$ K^{-1} at 205.8 K and 0.1 MPa, we obtain $E_V/H_P = 0.73 \pm 0.03$. This value is larger than the value for 7PGDE; thus, the presence of hydrogen bonding reduces the effect of volume. This is illustrated in Fig. 3, which shows the E_V/H_P ratio vs the degree of polymerization for a series of hydrogen bonded glycols including both the present results and literature data[30] [note that the glass transition temperature was defined as $\tau\,(T_g) = 0.01$ s in Ref. 30]. An increasing n corresponds to a lower density of terminal hydroxyl groups and thus a decreased degree of hydrogen bonding. This results in a correspondingly smaller ratio E_V/H_P, reflecting the progressively stronger influence of volume on the dynamics for the longer chains, opposite to the effect in normal polymers.[20] Also included in Fig. 3 is the value for 7PGDE, which is equivalent within the experimental error to the limiting value of E_V/H_P for the polymer polypropylene glycol with $n = 69$, for which the (sparse) end groups do not play a significant role in the dynamics.

We now investigate the third generality (iii) discussed above, namely, the decrease in fragility normally observed for increasing pressure. The isobaric fragility m_P is commonly used to characterize the increasing relaxation time on approach to the glass transition temperature T_g.[7] It has previously been reported[16] that m_P for 7PG increases with pressure in contrast to the normally observed decrease with P for non-hydrogen-bonded glass formers. In Fig. 4, we show the values of m_P calculated at each measurement pressure using the reported Vogel-Fulcher parameters;[16] to avoid extrapolation, we used $\tau(T_g) = 0.1$ s. The increase of m_P with pressure for 7PG is similar to that found both for lower molecular weight propylene glycols[30] and for other hydrogen bonded materials.[31] The pressure dependence of the fragility for 7PGDE is calculated using[4]

$$m_P = \frac{\Delta V}{\ln(10) RT dT_g/dP}, \tag{5}$$

in which ΔV $[= RT(d \ln \tau/dP)|_T]$ is the activation volume. As shown in Fig. 4, there is considerable scatter in the results since Eq. (5) involves two derivatives. Nevertheless, a trend of m_P decreasing with P is consistent with the data. Alterna-

tively, when Eq. (1) is valid, we can determine the fragility from the scaling exponent using[8]

$$m_P = m_V[1 + \gamma\alpha_P T_g], \tag{6}$$

where m_V is the fragility at constant volume. Since m_V is invariant to V (at fixed τ), we can use the value of m_P measured directly at ambient pressure to calculate the fragility at all higher pressures. This yields the solid line through the data in Fig. 4. The agreement is good between the two determinations, noting that the use of Eq. (6) significantly reduces the scatter in the data. The results shown in Fig. 4 demonstrate the dramatic effect that hydrogen bonding exerts on the pressure coefficient of fragility.

Referring to Eq. (5), it is intriguing that $dT_g/dP = 130 \pm 10$ K/GPa and $\Delta V = 147 \pm 8$ ml/mol [using $\tau(T_g) = 0.1$ s] for both 7PG and 7PGDE in the limit of zero pressure. The manifestations of H bonding become significantly more apparent with increasing pressure (see Fig. 4). There are two causes for this. First, since P and T have the opposite effect on τ, higher pressure measurements usually correspond to higher temperature measurements. The reduced influence of H bonding at higher T due to thermal dissociation speeds up the structural relaxation. Second, since an increased pressure reduces the available volume, directional bonds may be sacrificed to allow enhanced molecular packing (as is well known for water). These two effects, which are absent in nonassociated liquids, can bring about the observed breakdown of the otherwise general dynamical behaviors.

To conclude, we have shown that the failure of a hydrogen bonded system to conform to all three "generalities" of pressure dependent supercooled dynamics is removed when H bonding is eliminated. This work clearly shows that hydrogen bonding exerts a significant influence on the supercooled dynamics, and this influence is especially evident when pressure is used as an experimental variable.

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