ISOBARIC AND ISOCHORIC PROPERTIES OF GLASS-FORMERS

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Abstract. From new results for the equation of state of dibutylphthalate in combination with previously reported dielectric relaxation data, an analysis of the volume contribution to the dynamics was carried out for this fragile glass-former ($m_P = 84$). We find that the ratio of the isochoric and isobaric fragilities equals 0.75, the largest found to date for any molecular van der Waals liquids, reflecting a strong temperature effect, consistent with the large fragility. The relaxation times superpose when plotted versus temperature times the specific volume raised to the 3.2 power. This is a somewhat larger value of the exponent than expected based on the fragility of DBP. The implication is that for molecular glass-formers, the classical Lennard-Jones repulsive potential may represent the limit for fragile liquids.

Keywords: glass transition, pressure dependence, structural relaxation.

1. Introduction

Although the art of glass-making dates to ancient times and glasses are part of everyday life, efforts to understand the phenomenon at the molecular level continue unabated. The most spectacular change, and thus a primary focus of research, is the dramatic slowing down (by more than 14 decades) of molecular motions in a liquid during vitrification, which transpires without change in molecular arrangement and only modest (a few percent) changes in thermodynamic parameters such as T and V. The lack of any signature of the glass transition means that without a temporal reference, the

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molecular motions of a glass cannot be differentiated from those of the corresponding supercooled liquid. In light of this, much of the effort to understand the glass transition is devoted to finding correlations of the dynamics with other physical properties.

Here we report some new data for dibutylphthalate (DBP) and briefly review some results from the study of small molecular glass formers under high pressure.

2. Fragility and scaling

A popular metric for classifying the structural dynamics is the parameter m, referred to as the steepness index or the fragility[1,2]

$$m = \left.\frac{\partial \log(x)}{\partial (T_g/T)}\right|_{T=T_g} . \tag{1}$$

Here T_g is the glass transition temperature, often defined as $\tau(T_g) = 100\text{s}$, and x can be the viscosity or a relaxation time τ, with the latter measured by dielectric spectroscopy, photon correlation, neutron scattering, Brillouin scattering, or other experimental techniques. The fragility varies among small molecules and polymers in the range $35 \le m \le 214$,[3–7] indicating the drastic differences in dynamics among different materials. The fragility has been shown to depend on pressure, generally decreasing with increasing pressure,[8] apart for cases in which hydrogen bonds are present. Using the equation of state (EOS) it is possible to calculate the fragility for isochoric conditions (m_V). The ratio of m_V with the (more usual) isobaric fragility determined at atmospheric pressure (m_P) gives a direct measure of the relative importance of volume to the dynamics at atmospheric pressure. If τ is a unique function of volume, then $m_V = 0$ (no change of τ at constant V); conversely, $m_V = m_P$ if τ depends only on T. Of course, it follows that $0 \le m_V \le m_P$.

The isochoric fragility m_V can be determined from m_P using the relation[9,10]

$$m_P = m_V\left(1 + \gamma \alpha_P T_g\right), \tag{2}$$

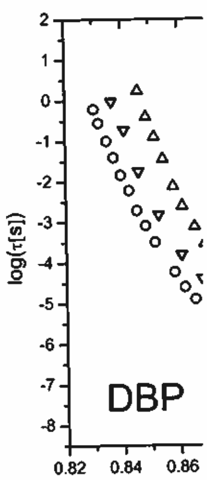
where α_P is the isobaric volume expansion coefficient and γ is a material constant, obtained from the scaling relation

$$\tau(T,V) = \Im\left(TV^{\gamma}\right). \tag{3}$$

The superposition of relaxation times when expressed as a function of TV^{γ} has been verified for many glass-formers from dielectric relaxation and other measurements.[9–17]

3. Results for DBP

For the case of DBP using published dielectric relaxation times[18] and new data on the EOS it is possible to determine the volume dependence of the relaxation time (Fig. 1)



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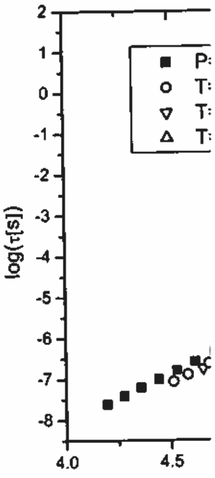

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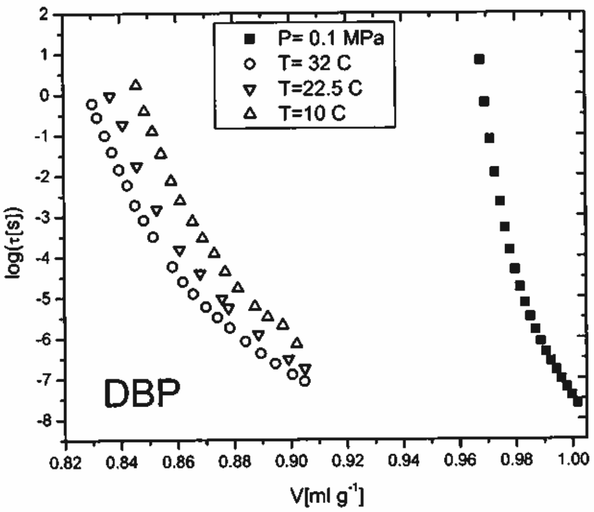

Figure 1. Dielectric relaxation time for DBP versus specific volume. The τ data are from Ref. 18.

and the relative importance of temperature and volume for the dynamics. From Fig. 1 it is evident that the dynamics of DBP is far from being a unique function of V. The relative dependence on T and V is also in this case well represented by the scaling (Eq. (3)). In Fig. 1, the $\tau(T,V)$ data fall all in a master curve when plotted versus the scaling variable TV^{γ} for $\gamma = 3.2$. The value of γ is the smallest value found so far for molecular glass formers without hydrogen bonds.

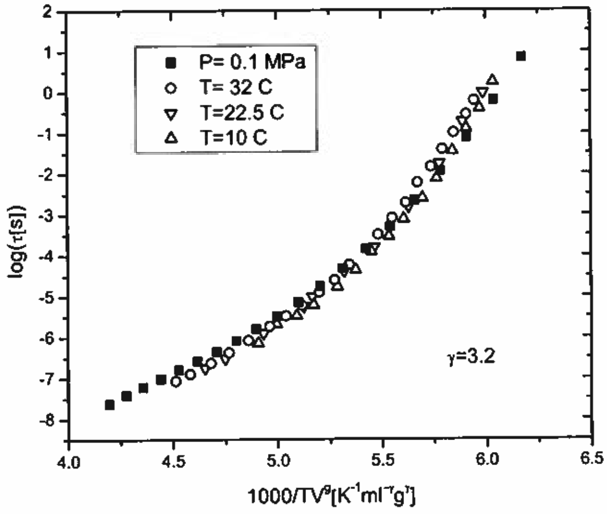

Figure 2. Dielectric relaxation times at $P = 0.1$ MPa (atmospheric pressure) and three fixed temperatures for DBP versus the product TV^{γ}.

From the data at atmospheric pressure, we determined the isochoric fragility $m_P = 83.8$ and $T_g = 177.4$ K. Knowing the isobaric fragility and the isobaric expansion coefficient $\alpha_P = 5.78 \times 10^{-4}\text{C}^{-1}$, using equation (2) it is possible to calculate the ratio of isobaric and isochoric fragility $m_V/m_P = 0.75$ and the isochoric fragility, $m_V = 63.1$. The large ratio m_V/m_P indicates that temperature plays a more important role than volume in the dynamics. For small molecule glass formers without hydrogen bonds the values of m_V/m_P have been found in the range $0.38 \le m_V/m_P \le 0.64$;[19] therefore, the value found for DBP is larger than any other found so far. This unusually large value of the ratio m_V/m_P correlates well with the rather small value of γ.

From data on various materials, including molecular and polymeric glass-formers, a correlation was found between m_V and m_P. $m_P = (33 \pm 4) + (0.92 \pm 0.05) m_V$.[20,21] An important consequence of this correlation is that large m_P is associated with large ratios of m_V/m_P; thus, temperature exerts a stronger relative effect on more fragile materials.

In Fig. 3 we report the isobaric versus isochoric fragility for 34 materials including DBP. The results or DBP seems to agree with the general correlation found previously however, the value of m_P is smaller than that observed for other materials having comparable m_V (or larger m_V for comparable m_P).

Finally we tested the correlation between the parameter γ and the isochoric fragility, by plotting (Fig. 4) γ versus the inverse isochoric fragility for DBP and comparing with the values found previously for other molecular glass formers. While in general m_V decreases with increasing γ, DHIQ and PC are outliers.

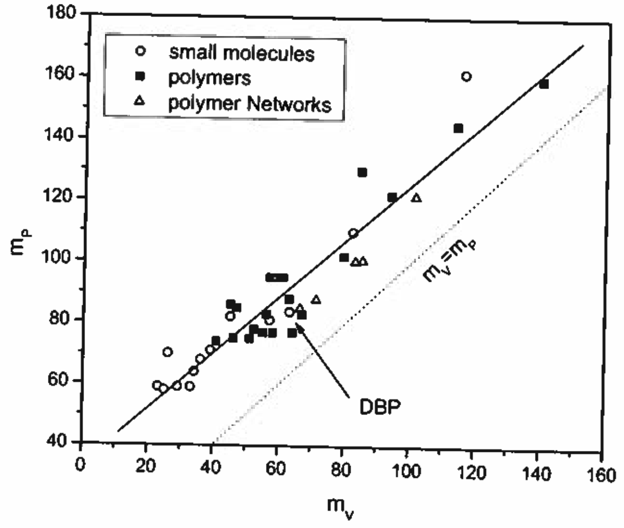

Figure 3. Isobaric fragility m_P (at atmospheric pressure) versus isochoric fragility m_V for 33 materials (in order of increasing m_V).[20]

The implication is that for molecular glass-formers, $\gamma \sim 4$ is a lower limit, rather than $\gamma = 0$. This result deserves further investigation on other fragile liquids.

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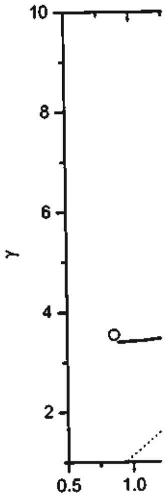

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The dependence of the relaxation time for DBP on volume and temperature shows some interesting features distinguishing it from other materials. The high isobaric fragility is associated with a high isochoric fragility; however; the value of m_V is somewhat higher than expected from the correlation between m_V and m_P established for most glass-formers (solid line in Fig. 4). This implies that volume has a less important role than expected for this fragile material. The importance of volume is also reflected in the value of γ, which is large in comparison to the scaling exponents found for comparably fragile materials (i.e., polymers and associated liquids[19]). But there is an important difference: for polymers, the small values of γ is due to the large fraction of intramolecular bonds, which are insensitive to pressure, thus minimizing the effect of V.[22] On the other hand, for a simple molecule like DBP, the small magnitude of γ reflects directly the nature of the intermolecular interactions.

The idea of using Eq. (3) to analyze relaxation times arose from the notion that for local dynamics, the intermolecular potential could be approximated by an inverse repulsive power law.[13,23] Such a potential is most appropriate for spherically symmetric molecules with a dominant repulsive part, with the scaling exponent γ then interpreted in terms of the exponent 3γ of the inverse power law potential. Certainly, molecular glass-formers lacking hydrogen bonds most closely approximate this ideal case. We find in Fig. 5 that the limiting value of γ approaches the value for the classical Lennard-Jones potential, $3\gamma = 12$.

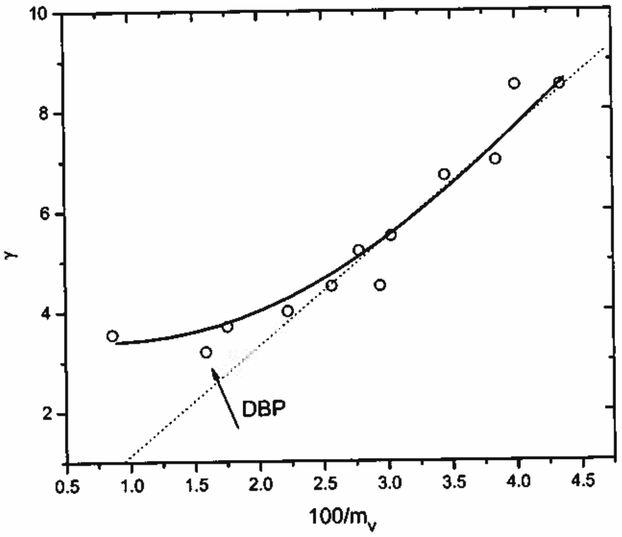

Figure 4. Parameter γ versus the inverse isochoric fragility for 12 amorphous materials. The small-molecule glass-formers (in order of increasing m_V) are: PCB62, BMMPC, BMPC, PCB54, PCB42, KDE, salol, PDE, OTP, PC, DBP, and DHIQ. The dashed line is a linear fit of all data including polymers [Ref. 20], while the solid line is a guide to the eye for the behavior of molecular glass-formers.

4. Summary

From PVT measurements on DBP in combination with previously published dielectric relaxation times, the relative contributions of temperature and volume (density) to the T-dependence of the structural relaxation dynamics were quantified. The ratio of the isochoric and isobaric activation enthalpies = 0.75, which is the highest value of m_V/m_P found to date for molecular glass-formers absent hydrogen bonding. Since DBP is not the most fragile molecular glass-former, this large value is somewhat at odds with the observation that a large m_V/m_P ratio corresponds to large m_P (or large m_V is associated with large m_P). The value of m_V, however, is somewhat larger than expected from the general correlation between m_V and m_P. This means that volume plays a less significant role than expected from correlations of these quantities.

The relaxation times are found to superpose onto a master curve when plotted as a function of $TV^{3.2}$. This exponent is larger than anticipated from the assumption that γ is inversely proportional to m_V (dotted line in Fig. 5). The suggestion is that for molecular glass-formers, γ tends to a limiting value ~4 for large m_V; further work is needed to confirm this. Assuming the exponent γ reflects the nature of the intermolecular repulsive potential, this limiting value of the exponent corresponds to the repulsive term in the classical Lennard-Jones 6–12 potential. Smaller values of γ have been found but only for polymers and hydrogen-bonded liquids.

Acknowledgments

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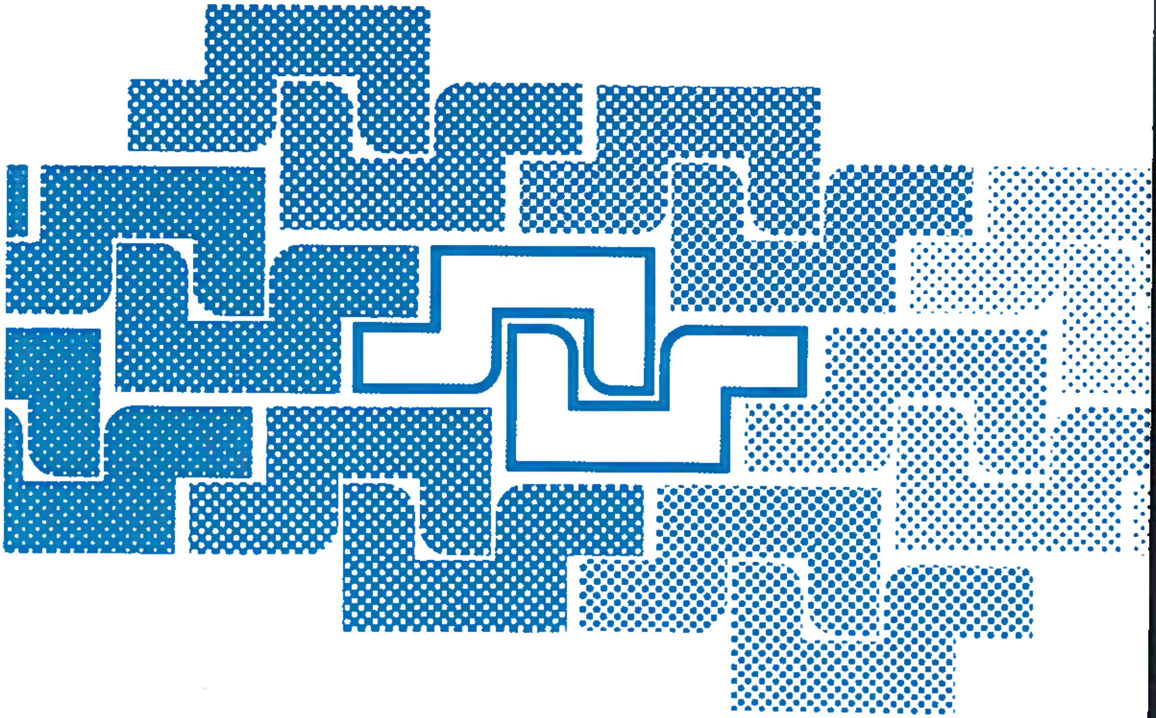

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