PHILOSOPHICAL MAGAZINE, 1 May–1 June 2004
VOL. 84, NOS. 13–16, 1573–1581

Volume and temperature as control parameters for the dielectric α relaxation of polymers and molecular glass formers

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ABSTRACT

Methods of analysing the dielectric α relaxation and equation-of-state data for supercooled glass-forming materials, to determine the relative contribution of volume and temperature, are illustrated using measurements on poly[(*o*-cresyl glycidyl ether)–co-formaldehyde] (PCGE). The ratio $E_V/E_P = 0.66$ of apparent activation energies and the ratio $|\alpha_\tau|/\alpha_P = 1.7$, of the thermal expansivities, evaluated at $\tau = 1\,\mathrm{s}$ and $P = 0.1\,\mathrm{MPa}$ respectively, reveal that for PCGE the volume and temperature both exert a substantial influence on the relaxation times. In this regard, PCGE is similar to other polymers and non-associated molecular liquids for which such analyses have been carried out. This means that the underlying bases of both free-volume and thermal activation models are not correct. The exceptional behaviour is that of hydrogen-bonded liquids, such as polyalcohols, for which competing effects minimize the sensitivity to pressure, whereby temperature becomes the dominant control variable.

§ 1. INTRODUCTION

The making of glass has been known for over five millennia, with applications ranging from works of art to practical artefacts. In the past century, the synthesis of new materials, particularly polymers, together with the availability of different routes for glass formation, have led to the utilization of glassy materials in virtually all

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Philosophical Magazine ISSN 1478–6435 print/ISSN 1478–6443 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/14786430310001644350

facets of everyday life. Notwithstanding the ubiquity and technological significance of glasses, a universally accepted physical description of how a liquid transforms into a glass is lacking.

As observed using various spectroscopies (mechanical, dielectric, light scattering, nuclear magnetic resonance and neutron), molecular motions in liquids became progressively slower upon approach to the glassy state, with a characteristic time τ increasing from nanoseconds to beyond feasible experimental durations. This leads to an operative definition of the glass temperature T_g as the temperature at which $\tau \approx 10\,\mathrm{s}$, the exact value of $\tau(T_g)$ varying for different spectroscopies. Of course, characteristic changes in physical properties, such as the heat capacity, volume and modulus are also used to define a T_g, which is close to the spectroscopic value. For non-isothermal experiments, T_g also depends on the rate at which the transition is approached.

One approach to describe the progressive slowing down of the dynamics focuses on the decrease of volume, which causes steric constraints (jamming) of the molecular motions. Models based on this idea, referred to as *free-volume* models, have a long history (Ferry 1980, Grest and Cohen 1981, Bendler *et al.* 2001). A converse viewpoint, from what are generally known as *landscape models*, describes the constraints in terms of progressive trapping within the potential energy surface. Reduced temperature decreases the energy available to surmount these potential barriers, and usually there is no explicit consideration of volume, and certainly not of free volume. Landscape models are widely employed in molecular dynamics simulations of glass formers (Goldstein 1969, Angell 1995, Sastry 2001).

The obvious difference between these two approaches is the thermodynamic quantity, either volume or temperature, considered to be the *control variable* for the glass transition. Ferrer *et al.* (1998), using literature results for triphenyl phosphate and glycerol, concluded ‘unambiguously that it is temperature, and not density, that is the overwhelmingly dominant control variable’. In a similar vein, Williams (1997) stated that ‘relaxation processes arise from molecular motions that are driven by temporal fluctuations in thermal energy … not a time-averaged quantity such as free volume’. However, based on dielectric spectroscopy measurements at an elevated pressure, we have reached a very different conclusion (Paluch *et al.* 2002a), namely that an emphasis on temperature understates the role of volume, at least for non-associated glass formers.

From a theoretical perspective, the dichotomy is not so great. The potential energy barriers at the heart of landscape models are affected by the density, and variations on free-volume models have been proposed, which incorporate temperature dependences into the model parameters (Macedo and Litovitz 1965, Pakula 2000). We also point out that the mode-coupling theory of the glass transition (Götze 1991), which expresses the dynamics in terms of the density correlation function, is based on a static structure factor governed by both temperature and density. Similarly, the coupling model of Ngai (2001), which addresses the consequences of intermolecular constraints on motion in dense phase, makes no attempt to quantify the specific role of density or temperature in governing the magnitude of these constraints. Thus, most existing models of the glass transition are not *a priori* incompatible with a varying influence from temperature or volume.

Assessing the relative importance of different thermodynamic variables requires measurements beyond standard conditions. Although there is a vast array of structural relaxation time data in the literature, these have almost always been measured as a function of temperature. Since changes in temperature affect not only the thermal energy but also the density, quantifying the relative contribution of these two variables cannot be achieved from temperature studies alone. Accordingly, there is increasing use of pressure as an experimental parameter, including studies by dynamic light scattering (Li *et al.* 1995, Comez *et al.* 2002, Paluch *et al.* 2003c), calorimetry (Takahara *et al.* 1999), inelastic neutron scattering (Tolle *et al.* 1998, Frick and Alba-Simionesco 1999), viscosity measurements (Schug *et al.* 1980, Cook *et al.* 1993), as well as simulations (Middleton and Wales 2003). However, the most popular technique for experiments at elevated pressure is dielectric spectroscopy (Williams 1997, Floudas 2003, Roland and Paluch 2003), because of experimental convenience and the ability to obtain data routinely over 12 decades of frequency. The variation in the α-relaxation time with both temperature and pressure can be determined. Using equation-of-state data, this information enables the isothermal volume dependence, together with the temperature dependence at fixed volume, of the relaxation times to be calculated. From this, an assessment can be made of the relative contributions of temperature and density.

In the following, we present new experimental results on poly[(*o*-cresyl glycidyl ether)–co-formaldehyde] (PCGE) and utilize these to illustrate the analysis of temperature and volume effects on structural (α) relaxation. We then offer a discussion concerning the relative importance of these two factors, and how differences in behaviour can be related to the chemical structure of the glass former.

§2. Experimental details

The PCGE was obtained from Aldrich and used without further purification. The material could be quenched below its crystalline melting point (about 345 K) into a completely amorphous state near T_g (= 285 K at ambient pressure). For dielectric measurements, the sample was placed between parallel plates inside a manganin pressure cell (Harwood Engineering). Dielectric spectra of the α relaxation were obtained with an IMASS time domain dielectric analyser (10^{-4} to 10^4 Hz) and a Novocontrol alpha analyser (10^{-2}–10^6 Hz). Pressure *P*–volume *V*–temperature *T* measurements utilized a Gnomix apparatus (Zoller and Walsh 1995).

§3. Results

The dielectric spectrum of PCGE was measured for pressures up to 260 MPa at $299\,\text{K} < T < 334\,\text{K}$. The relaxation time, defined as the inverse (circular) frequency of the maximum in the dielectric loss, increases progressively with increasing pressure and decreasing temperature *T*. We express τ as a function of specific volume, using the *P*–*V*–*T* measurements on this material. For each *T*–*P* pair, *V* is calculated, using the Tait equation of state (Zoller and Walsh 1995) to interpolate the data

$$V(T,P) = (v_0 + v_1 T)\left[1 - 0.0894 \ln\left(\frac{1+P}{b_0 \exp(-b_1 T)}\right)\right]. \qquad (1)$$

The best-fit parameters to the *P*–*V*–*T* data on PCGE are $v_0 = 0.705\,\text{ml}\,\text{g}^{-1}$, $v_1 = 4.855 \times 10^{-4}\,\text{ml}\,\text{g}^{-1}\,\text{C}^{-1}$, $b_0 = 234.7\,\text{MPa}$ and $b_1 = 3.4 \times 10^{-3}\,\text{C}^{-1}$. The results for $\tau(V)$ are shown in figure 1 (a).

The fact that volume does not uniquely define the relaxation time is not, in and of itself, an indictment of free-volume models. The requisite quantity is the free volume, which can be extracted from equation-of-state data using, for example, lattice models (Paluch *et al.* 2003a). The variation in τ with *V* in figure 1 (a) is greater

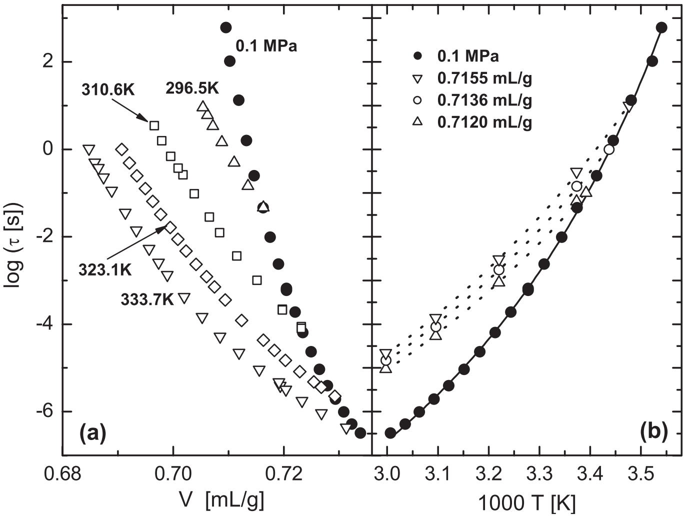

Figure 1. (a) Isotherms (△, □, ◇, ▽) and isobar (●) of α-relaxation times for PCGE as a function of specific volume. (b) Arrhenius plot of relaxation times for the indicated fixed volumes (▽, ○, △) and at constant pressure (●).

at fixed P ($=0.1$ MPa) than at fixed temperature, since the temperature alters both the thermal energy and the volume, whereas the pressure only affects the latter. By taking constant-volume intersections of the curves in figure 1 (a), we can obtain the temperature dependence of τ at fixed volume.

These are shown in figure 1 (b) where it can be seen that the curve for $\tau(T)$ at constant V is less steep than the temperature-dependence of τ measured at constant (atmospheric) pressure. As first pointed out by Hoffman *et al.* (1966), the constant-volume apparent activation energy

$$E_V(T, V) = R \left. \frac{\partial(\ln \tau)}{\partial T^{-1}} \right|_V$$

is invariably less than the constant-pressure activation energy

$$E_P(T, P) = R \left. \frac{\partial(\ln \tau)}{\partial T^{-1}} \right|_P .$$

This is problematic for free-volume theories, since it requires a decrease in the occupied volume with increasing temperature (Williams 1997). The ratio E_V/E_P yields a direct measure of the relative contribution of temperature and volume to the relaxation times (Naoki *et al.* 1987, Williams 1997). From the data in figure 1 (b), we obtain $E_V/E_P = 0.64$ for $V = 0.714\,\mathrm{ml\,g^{-1}}$ (corresponding to $\tau = 1$ s at atmospheric pressure). This ratio varies by less than 10% when evaluated at a value of τ one decade higher or lower.

Naoki *et al.* (1987) have shown that E_V/E_P can also be calculated from the relation

$$\frac{E_V}{E_P} = 1 - \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_\tau , \tag{2}$$

where $(\partial P/\partial T)_V$, calculated from the P–V–T data, equals $1.68\,\mathrm{MPa\,K^{-1}}$ at $V = 0.714\,\mathrm{ml\,g^{-1}}$ for the PCGE. The quantity $(\partial T/\partial P)_\tau$ is just the pressure coefficient of T_g; for PCGE, we obtain $\mathrm{d}T_g/\mathrm{d}P = 0.20\,\mathrm{K\,MPa^{-1}}$ for $\tau = 1\,\mathrm{s}$. From equation (2), $E_V/E_P = 0.66$, which is consistent with the determination using the τ in figure 1 (b).

As discussed by Ferrer *et al.* (1998), the relative dominance of temperature and volume is also reflected in the ratio of the constant-pressure thermal expansion coefficient $\alpha_P = V^{-1}\,(\partial V/\partial T)_P$ to the constant-relaxation-time thermal expansion coefficient $\alpha_\tau = V^{-1}\,(\partial V/\partial T)_\tau$. For PCGE at $P = 0.1\,\mathrm{MPa}$, $\alpha_P = 6.80\times10^{-4}\,\mathrm{C^{-1}}$ for the liquid near T_g, and we calculate, for $\tau = 1\,\mathrm{s}$, that $\alpha_\tau = -1.16\times10^{-3}\,\mathrm{C^{-1}}$. These in turn give $|\alpha_\tau|/\alpha_P = 1.7$.

§4. DISCUSSION

Two metrics for the roles of volume and temperature were calculated. The ratio of the isochoric to isobaric activation energies will fall between zero and unity, with a higher value connoting greater significance of temperature relative to volume. For PCGE at $\tau = 1\,\mathrm{s}$, $E_V/E_P = 0.65 \pm 0.01$, indicating that both quantities exert a substantial effect, with temperature slightly more dominant. This conclusion is corroborated by the ratio of the expansivities, $|\alpha_\tau|/\alpha_P = 1.7$. A ratio close to unity signifies that volume and temperature have equal significances, while a much larger value means that temperature is the primary control variable.

The results for PCGE are quite similar to those for other polymeric glass formers. In table 1 we have collected data for various glass formers, both molecular and polymeric. The calculations were made for $\tau = 1$, except for results from the older literature, which are for higher temperatures (higher frequencies). Taking those materials for which both E_V/E_P and $|\alpha_\tau|/\alpha_P$ are available, we plot the two ratios against each other in figure 2. A correspondence between the two quantities is evident, and in fact they are mathematically related (Casalini and Roland 2003). The intersection of the dotted lines in the figure denotes the boundary between the two regimes: relaxation governed by volume or by thermal energy. It can be seen that most materials fall in the middle of the range; that is, both parameters exert significant effects. The only exception is sorbitol.

The two poly(alcohols), sorbitol and glycerol, are the only glass formers in table 1 for which temperature is the dominant control parameter. This exceptional behaviour is the consequence of their hydrogen bonding. Thermal energy reduces the degree of hydrogen bonding, enhancing the direct effect that temperature has on the relaxation times. On the other hand, higher pressure also reduces hydrogen bonding (Naoki and Katahira 1991, Cook *et al.* 1992, Poole *et al.* 1994), since a smaller volume makes directional interactions more difficult. This serves to enhance molecular mobility, countervailing the direct effect of pressure on τ. The consequences are twofold: structural relaxation in associated liquids is less sensitive to pressure (smaller activation volumes and smaller $\mathrm{d}T_g/\mathrm{d}P$), and the magnitude of τ in the supercooled regime is governed primarily by temperature.

For non-associated glass formers, on the other hand, volume exerts a substantial effect (table 1), in some cases being even more important than thermal energy (i.e. $E_\mathrm{V}/E_\mathrm{P} < 0.5$ and $|\alpha_\tau|/\alpha_P < 1$). We can compare the fragility, defined as $m = \mathrm{d}\log(\tau)/\mathrm{d}(T_g/T)|_{T=T_g}$, with the relative magnitude of the effect that the volume has on τ. Since greater fragility implies greater deviation from Arrhenius behaviour (and more intermolecularly cooperative relaxation), it is of interest to see whether larger m correlates with smaller values of E_V/E_P and $|\alpha_\tau|/\alpha_P$. In figure 3, fragility is

Table 1. Thermal expansivity and activation energy ratios for $\tau = 1$ s.

Glass former	Abbreviation in figure 2	T_g (K)	$\lvert\alpha_\tau\rvert/\alpha_P$	E_V/E_P	References
1,1′-bis(*p*-methoxyphenyl)cyclohexane	BMPC	243	0.58	0.39	Paluch *et al.* (2003b)
1,1′-di(4-methoxy-5-methylphenyl)cyclohexane	BMMPC	263	0.72	0.41	Paluch *et al.* (2003b)
Salol		220	1.6	0.43	Casalini *et al.* (2003)
Cresolphthalein–dimethyl ether		313	0.98	—	Paluch *et al.* (2002b)
Phenolphthalein–dimethyl ether	PDE	249	1.25	0.53	Paluch *et al.* (2002a)
o-terphenyl	OTP	244	1.6	0.55	Naoki *et al.* (1987), Dreyfus *et al.* (2003)
Poly(propylene oxide)		198	—	0.55^a	Williams (1965)
Poly(styrene)	PS	373	1.7	0.64	Roland and Casalini (2003b)
Diglycidyl ether of bisphenol		335	1.8	0.6	Paluch *et al.* (2003c)
Poly(vinyl acetate)	PVAc	311	1.8	0.6	Roland and Casalini (2003a)
Poly[(phenyl glycidyl ether)–co-formaldehyde]	PPGE	258	1.7	0.63	Paluch (2002a)
Poly[(*o*-cresyl glycidyl ether)–co-formaldehyde]	PCGE	285	1.7	0.65	This work
Poly(vinyl methyl ether)	PVME	251	2.1	0.69	Casalini and Roland (2003)
1,2-poly(butadiene)		253	2.8	0.70	Roland *et al.* (2003)
Poly(methyl acrylate)		276	—	0.78^a	Williams (1964)
Sorbitol		273	6	0.87	Hensel-Bielowka *et al.* (2002)
Glycerol		189	17	—	Ferrer *et al.* (1998)

${}^a\tau \ll 1$ s.

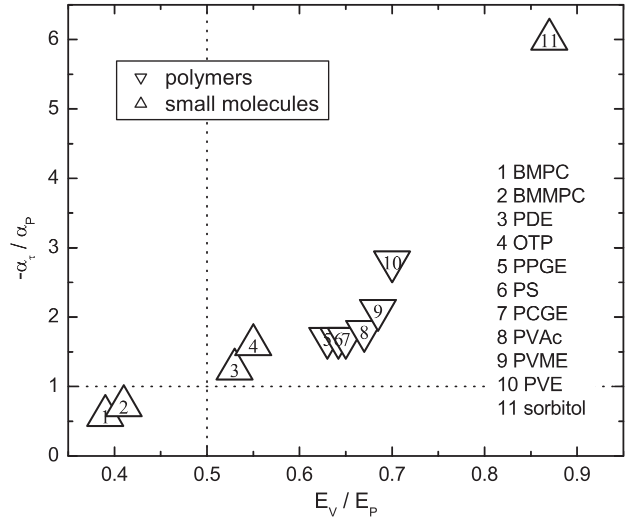

Figure 2. Ratio of thermal expansivities versus ratio of apparent activation energies for some of the glass formers in table 2. The intersection of the dotted lines denotes equal contributions from volume and temperature.

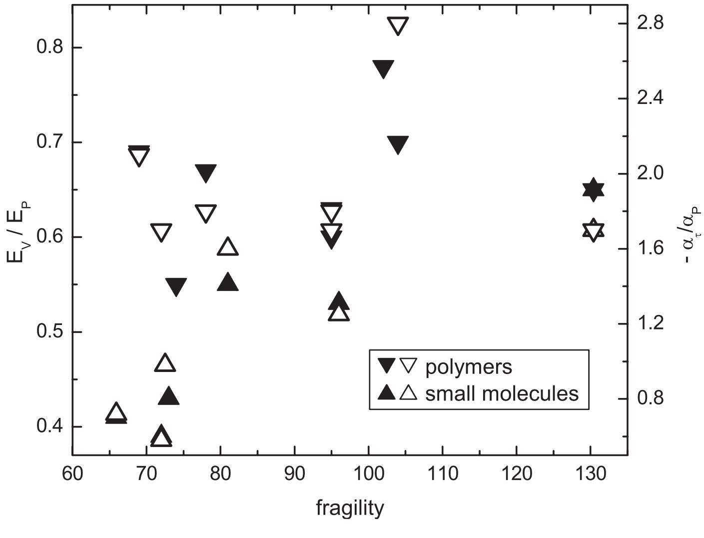

Figure 3. Ratio of apparent activation energies (▼, ▲) and ratio of thermal expansivities (▽, △) as functions of the isobaric fragility: (▽), (▼), polymers; (△), (▲), small molecules.

plotted versus E_V/E_P and $|\alpha_\tau|/\alpha_P$ for all glass formers in table 1, except for the hydrogen-bonded liquids. No general correlation is observed, although for molecular liquids the relative contribution of temperature to the relaxation times may increase weakly with increasing sensitivity of τ to T_g-scaled temperature. For the polymers, the data are more scattered, and no correlation is evident. Since the apparent isochoric and isobaric activation energies differ from the respective fragilities only by a constant factor (T_g times the gas constant), this means that the isochoric fragility bears no relationship to m for isobaric conditions, contrary to the findings of Huang *et al.* (2002) based on more limited data.

§ 5. CONCLUSIONS

PCGE is found to be similar to other polymers and molecular glass formers, in that neither temperature nor volume is the dominant control variable, at least in the absence of extensive hydrogen-bonding. This result is based on the analysis of dielectric relaxation measurements, in combination with equation-of-state data, for temperatures just above T_g. The fact that volume is not the dominant control variable is at odds with free-volume models of the glass transition, and the fact that temperature does not dominate undermines thermal activation models, including the entropy theory of Adam and Gibbs (1965). We also find that more thermally activated dynamics (i.e. a stronger role of thermal energy) is not associated with more Arrhenius-like behaviour.

ACKNOWLEDGEMENTS

The work at the Naval Research Laboratory was supported by the Office of Naval Research. M.P. thanks the Komitet Badan Naukowych, Poland (grant 2PO3B 022 20), for financial support.

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