On the isothermal pressure behaviour of the relaxation times for supercooled glass-forming liquids

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Abstract. This paper discusses the isothermal pressure behaviour of the relaxation times for supercooled glass-forming liquids. Analysis based on reference data and the authors' measurements of dielectric relaxation is carried out for both *strong* and *fragile* glass formers. All of the experimental relaxation times clearly exhibit a non-Arrhenius behaviour well reproduced by a function $\tau = \tau_{0p} \exp(C_p P/(P_0 - P))$ or $\tau = \tau_0 \exp(C P_0/(P_0 - P))$, giving the same estimates of the ideal glass transition pressure P_0. Experimental data indicate that *fragile* materials show a more rapid increase of the relaxation time with rise of pressure than the *strong* ones.

1. Introduction

One of the most striking features of supercooled liquids is the strong increase of the characteristic relaxation time, which reflects the underlying motion of molecules, with temperature decrease. It has been established that well above the glass transition temperature the evolution of the α-relaxation parametrizes the empirical Vogel–Fulcher–Tammann (VFT) equation [1]:

$$\tau = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right). \tag{1}$$

The material-dependent parameter D makes it possible to distinguish two main groups of glass formers: *fragile* ones (with small D-values, typically $D < 10$) and *strong* ones (with large D-values) [2–4]. *Strong* glasses turn out to exhibit an almost Arrhenius behaviour of the $\tau(T)$ dependence:

$$\tau = \tau_0 \exp\left(\frac{E_A}{kT}\right) \tag{2}$$

where E_A denotes activation energy. The VFT equation is formally transformed to an Arrhenius law for $T \gg T_0$.

The divergence of the relaxation time predicted by the VFT law at a temperature T_0, which is well above 0 K, is still a matter of continuous debate [5–11]. Due to the limited range of measured relaxation times, the ideal glass temperature T_0 has to be extrapolated. This extrapolation is based on data points which are far away from T_0. The question of whether T_0 is a true physical temperature still remains open. The extensive discussion of the applicability of these and other formulae describing the temperature dependence of the relaxation times can be found in references [12–15]. Undoubtedly, for a better understanding of the nature of the glass transition, new experimental facts are required. One possible

source is high-pressure studies, which offer an alternative way of approaching the glass state. Although pressure and temperature are generally treated as equivalent thermodynamic parameters, they have different effects on the relaxation process. Temperature mainly influences processes associated with the activation energy (e.g. excitation of rotational energy states) whereas pressure leads to changes in intermolecular distances. Due to the relatively weak molecular interactions in typical complex liquids, one can expect even a moderate pressure of few hundred MPa to be possibly sufficient to induce significant changes of molecular properties. Worth stressing is the agreement of the data, obtained in the isothermal pressure studies, with the *free-volume* model [16, 17].

On the whole, this indicates that high-pressure studies play an essential role in obtaining an understanding of the properties of the vitrification processes in liquids [18–20]. Nevertheless, such experiments are still rare in comparison with temperature studies under atmospheric pressure. This is partially due to technical problems encountered when the high pressure route is adopted and partially due to deficiencies in the corresponding theoretical treatments. The introduction of pressure as a variable into the study of the molecular mobility in supercooled liquids results in volume playing a primary role in the relaxation process.

Dielectric relaxation of supercooled liquids at elevated pressures has been extensively investigated by Naoki and co-workers [21–23]. The dynamical properties of glass-forming liquids have been analysed in terms of activation variables and configurational quantities. Naoki *et al* [23] found that in orthoterphenyl (OTP), $\tau(T)$ behaviour, for a few different iso-bars ($P = 0.1$ MPa, 19.6 MPa, 39.2 MPa, 58.2 MPa and 78.5 MPa), can be parametrized by means of the VFT equation, assuming that the pressure dependence of B and T_0 is linear. They determined the following values of B and T_0: $B = 3779 + 3.43P$ and $T_0 = 170 + 0.19P$.

The pressure evolution of the relaxation time has been frequently analysed by means of the pressure version of the Arrhenius relation [21, 24], namely

$$\tau = \tau_A \exp\left(\frac{PV^*}{RT}\right) \tag{3}$$

where V^* is the activation volume.

Experimental data spanning about three decades of relaxation times, obtained for OTP (in the pressure range from 0.1 MPa up to 80 MPa) using specific heat spectroscopy, can be well described with the above formula (equation (3)) [25].
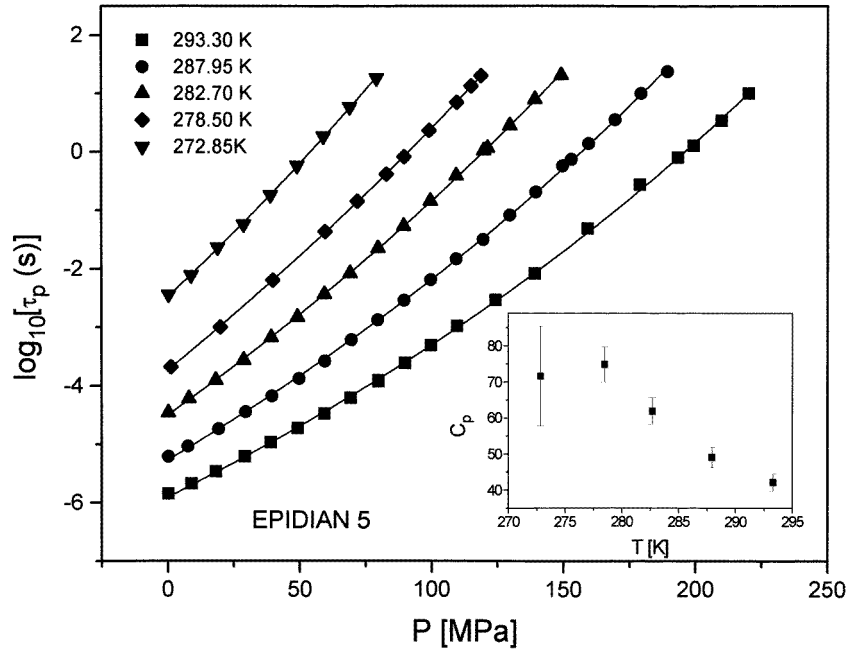
Recently [26], pressure dielectric relaxation measurements on iso-dibutyl phthalate (moderately fragile glass formers) were effectively described by a functional form iso-morphic to the VFT relation (1), namely

$$\tau = \tau_0 \exp\left(\frac{B}{P_0 - P}\right) \qquad T = \text{constant} \tag{4}$$

which can be derived from the free-volume model [27], applying the Doolittle formula. Note that P_0 (the pressure of an ideal glass transition) is explicitly involved in equation (4). In reference [28], however, on the basis of isothermal pressure measurements of the dielectric relaxation in glycerol (a 'classical' *strong* glass former), another expression was proposed:

$$\tau = \tau_{0p} \exp\left(\frac{C_p P}{P_0 - P}\right) \qquad T = \text{constant}. \tag{5}$$

Interestingly enough, for $P \ll P_0$ this equation takes the form of the pressure Arrhenius relation.
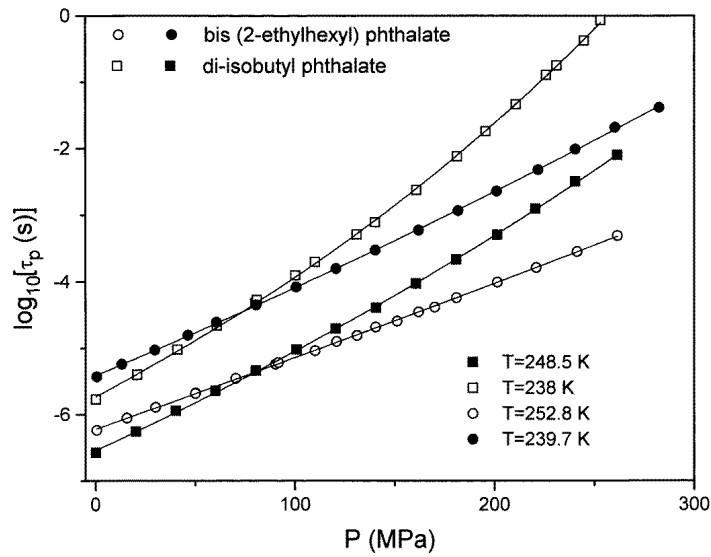
Figure 1. Pressure dependencies of the logarithm of the dielectric relaxation times for Epidian 5 (EP 5) for a few isotherms presented in the figure. The inset shows the temperature dependence of the fitted parameter C_p (relation (5)).
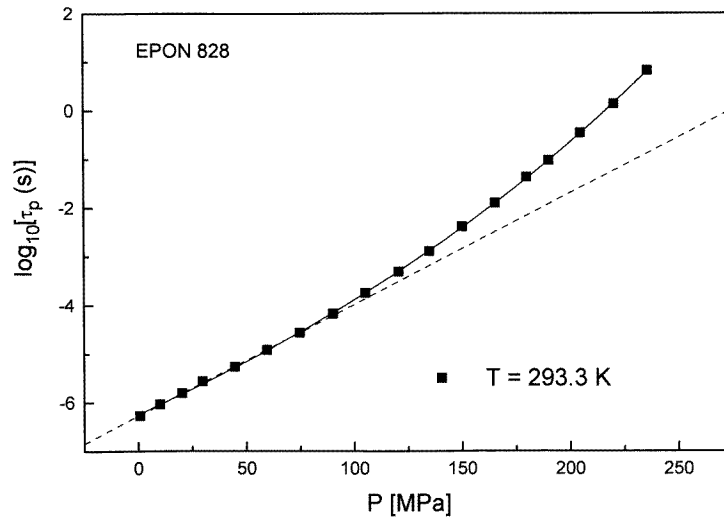
**Figure 2.** The pressure dependence of $\log_{10}[\tau/s]$ for Epon 828 (EP 828). The dashed line represents the Arrhenius law.

Below, we discuss the isothermal pressure dependence of the dielectric relaxation times for glass-forming liquids ranging from *fragile* to *strong*. It seems that the classification of glass formers based on the value of the 'fragility parameter', which was derived by Angell

Figure 3. Pressure dependencies of $\log_{10}[\tau/s]$ for bis(2-ethylhexyl) phthalate (BEP) and di-*iso*butyl phthalate (DBP) for a few isotherms given in the figure.
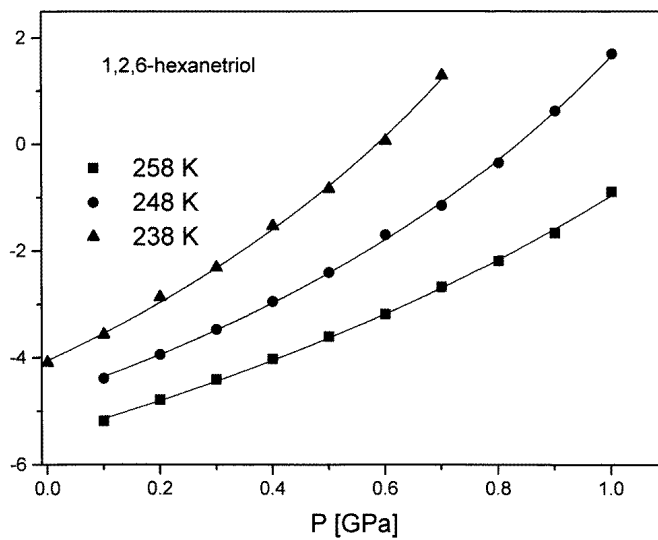
Figure 4. The logarithm of the relaxation time as a function of pressure for 1, 2, 6-hexanetriol (HXL) (data taken from [32]).

et al [2–4] from experimental temperature data, cannot be generalized for the pressure behaviour of τ. The analysis is based on experimental results available in the literature as well as the authors' previous and new experimental data. New measurements were carried out for low-molecular-weight liquid diglycidyl ether of bisphenol-A (Epon 828) with an epoxy equivalent weight of about 190.

The experimental technique was described in detail in our previous papers [26, 28, 29].
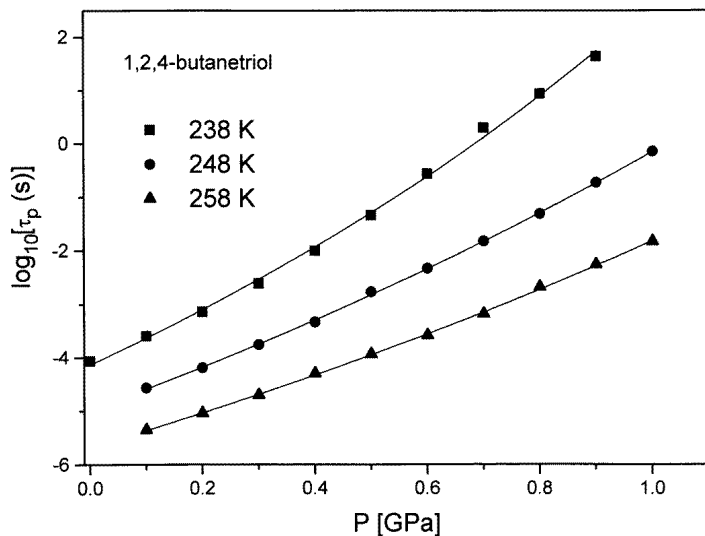
Figure 5. The logarithm of the relaxation time $\log_{10}[\tau/s]$ versus pressure in 1, 2, 4-butanetriol (BTL) (data taken from [33]).
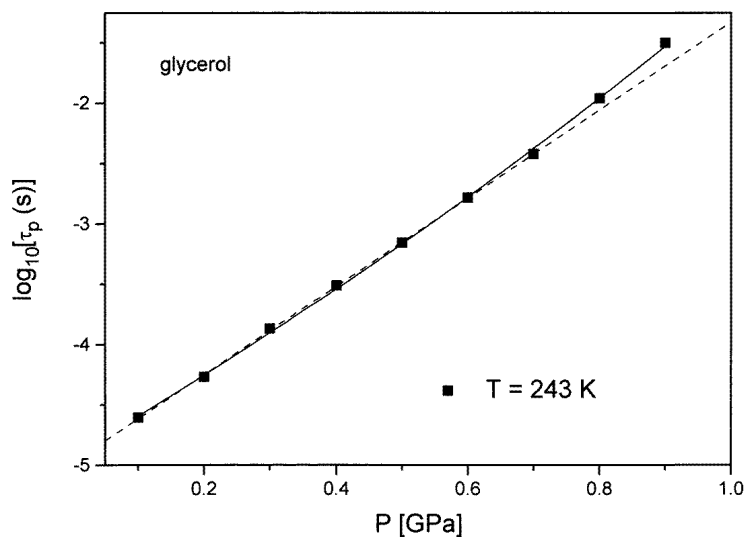
Figure 6. The isothermal pressure dependence of the relaxation times for glycerol (GL). The dashed straight line represents the Arrhenius law (data taken from [24]).

2. Results and discussion

Figures 1, 2 and 3 present the results of our studies of dielectric relaxation for Epidian 5 (figure 1) (reference [30]), Epon 828 (figure 2) and bis(2-ethylhexyl) phthalate (reference [31]), di-isobutyl phthalate (figure 3) (reference [26]), while figures 4, 5 and 6 show the isothermal pressure behaviour of the dielectric relaxation times for 1, 2, 6-hexanetriol (reference [32]), 1, 2, 4 butanetriol (reference [33]) and glycerol (reference [24]). The

experimental data are ordered to cover the range from a very *fragile* system (Epidian 5, $D = 6$) to a *strong* glass former (glycerol, $D = 16$) and the sequence of figures correspond to the shift of the fragility parameter D. The data presented clearly show a non-Arrhenius behaviour of the relaxation times for all of the liquids.

Table 1. Fitting parameters for the data shown in figures 1–6, using the equations $\tau = \tau_{0p} \exp[C_p P/(P_0 - P)]$ and $\tau = \tau_0 \exp[C P_0/(P_0 - P)]$.

Glass former	T (K)	P_0 (MPa)	C_p, C^{a} (no units)	$\log_{10}[\tau_0/\mathrm{s}]$	$\log_{10}[\tau_{0p}/\mathrm{s}]$	$\log_{10}[\tau/\mathrm{s}]$ for $P = 0.1$ MPa[b]
EP 5 (figure 1)	293.30	802 ± 31	42 ± 2.5	-24.1 ± 1	-5.899 ± 0.020	-5.846
$D = 5.7$	287.95	789 ± 32	49 ± 2.5	-26.5 ± 1.1	-5.260 ± 0.017	-5.206
	282.70	835 ± 40	62 ± 3.5	-31.4 ± 1.5	-4.489 ± 0.012	-4.456
	278.50	885 ± 50	75 ± 5	-36.2 ± 2.1	-3.719 ± 0.011	-3.67
	272.85	733 ± 127	72 ± 14	-33.5 ± 6	-2.469 ± 0.017	-2.438
EP 828 (figure 2)	293.3	737.4 ± 15	34 ± 1	-21.3 ± 0.5	-6.236 ± 0.012	-6.272
DBP (figure 3)	248.5	1462 ± 100	47 ± 4	-26.9 ± 1.7	-6.540 ± 0.014	-6.575
$D = 9.7$	238.00	895 ± 29.8	33 ± 2	$-20. \pm 0.7$	-5.727 ± 0.016	-5.768
BEP (figure 3)	252.8	5270 ± 1170	133 ± 33	-61.7 ± 13	-6.214 ± 0.007	-6.232
$D = 11.6$	239.7	2450 ± 225	72 ± 7	-36.5 ± 3.2	-5.411 ± 0.010	-5.427
HXL (figure 4)	258	3170 ± 300	23 ± 3	-15.2 ± 1.4	-5.451 ± 0.046	—
	248	2320 ± 100	19 ± 2	-13.2 ± 0.7	-4.726 ± 0.046	—
	238	2030 ± 220	23 ± 4	-14.1 ± 1.7	-4.050 ± 0.060	-4.09
BTL (figure 5)	258	5390 ± 720	39 ± 6.5	-22.6 ± 2.8	-5.676 ± 0.029	—
$D = 10.2$	248	5050 ± 510	45 ± 6	-24.6 ± 2.5	-4.975 ± 0.030	—
	238	3590 ± 650	40 ± 10	-21.6 ± 4.2	-4.128 ± 0.073	-4.06
GL (figure 6) $D = 16$	243	628 ± 1510	47 ± 13	-25.2 ± 5.7	-4.917 ± 0.035	—

[a] The standard errors for parameter C are twice the size of those for parameter C_p.
[b] The values of the relaxation time at atmospheric pressure (obtained from the isothermal measurements) have been included for comparison.

Moreover, we noted that for fragile glass formers the increase of the relaxation times with pressure is definitely stronger than that for the strong ones (cf. figures 1 and 6). The qualitative analysis of the experimental data was conducted using relations (4) and (5). However, it is convenient to apply relation (4) rewritten in a form identical to that of the VFT relation (1):

$$\tau = \tau_0 \exp\left(\frac{C P_0}{P_0 - P}\right) \tag{6}$$

i.e. introducing explicitly the dimensionless parameter C, similarly to the parameter D accounting for fragility in studies under atmospheric pressure. The results of these analyses are given in table 1. It is noteworthy that for the range of relaxation times for which tests were made, from 10^{-2} to 10^7 s, both equations, (5) and (6), represent very well the experimental data presented, following the same solid lines in figures 1–6 and giving the same estimates for P_0 (table 1). Worth noticing is the large discrepancy between the values of the relaxation times τ_0 and τ_{0p} in relations (6) and (5). The latter is equal to the value of the relaxation time under atmospheric pressure for a given temperature. However, the

relation between these pre-exponential factors can be easily shown analytically:

$$\tau = \tau_{0p} e^{-C}. \tag{7}$$

Fitting of relations (5) and (6) gives, within the limit of the experimental error, the same value of the dimensionless parameter C—the pressure analogue of the 'fragility' parameter D. However, the results presented in table 1 clearly show that there is no correlation between the degree of fragility determined from measurements under atmospheric pressure and the coefficient C. In fact, the value of C is almost the same for glycerol (figure 6), where the pressure of 1000 MPa shifts the relaxation times down by three orders of magnitude, and for Epidian 5 (figure 1), where the same occurs for 100 MPa. The value of C seems to increase systematically only when the temperature of the isotherm tested decreases (see the inset in figure 1 and table 1).

3. Conclusions

The analysis presented above shows that the isothermal pressure behaviour of relaxation times may be described in a similar way to the temperature behaviour under atmospheric pressure (by the VFT-type relations (6) and (1), respectively). In this context, T and P can be regarded as equivalent thermodynamical variables in the vitrification process. The equivalence of the temperature and pressure paths for approaching the glassy state has also been indicated in computer simulation studies of one- and two-component mixtures with an inverse-power pair potential [34, 35]. In 1980 [34], it was stated that the free-volume values for which the glass transition occurs are the same for the two ways of approaching the glassy sate. A recent molecular dynamics simulation of a pressure-induced glass transition in a Lennard-Jones liquid shows that the glass has essentially the same structure on cooling or squeezing [35].

However, this similarity does not extend to the parameters D and C. The comparison of their values (table 1) may lead to the conclusion that the fragility of a given material is linked with the activation energy of the microstructures rather than with the changes of the intermolecular distances or the available free volume.

For all of the materials on which tests were conducted, which are characterized by different fragilities, different chemical structures and different intermolecular interactions, a non-Arrhenius pressure behaviour of τ was found on approaching the glass transition. It seems that this type of $\tau(P)$ behaviour in the vitrification process can be regarded as universal in view of the diversity of the materials considered. Up to now, the Arrhenius form (equation (3)) has often been applied to analyse the $\tau(P)$ behaviour. However, its eventual validity is limited to just a narrow range of pressures, at large distances from P_0. When discussing the non-Arrhenius behaviour, the applicability of relation (5) is particularly noteworthy. It is the only formula which includes two adjustable parameters, P_0 and C: the value of the pre-exponential coefficient τ_{0p} can be taken from temperature studies under atmospheric pressure. This makes fitting the experimental data easy even for *strong* glass formers. Its consistency with the Arrhenius relation, for $P \ll P_0$, offers the possibility of obtaining a coherent description of both the non-Arrhenius and Arrhenius regions. Such a function has not yet been found for the isobaric temperature behaviour of relaxation times. Unfortunately, the verification of this hypothesis requires dielectric studies at frequencies much higher than 10 MHz, which to the authors' knowledge have not as yet been carried out.

Acknowledgments

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