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# The dynamics crossover region in phenol- and cresol-phthalein-dimethylethers under different conditions of pressure and temperature

Riccardo Casalini<sup>1,3</sup>, Marian Paluch<sup>1,2</sup> and C Michael Roland<sup>1</sup>

<sup>1</sup> Naval Research Laboratory, Chemistry Division, Code 6120, Washington, DC 20375-5342, USA

<sup>2</sup> Institute of Physics, Silesian University, Uniwersytwcka 4, 40-007, Poland

E-mail: [casalini@ccs.nrl.navy.mil](mailto:casalini@ccs.nrl.navy.mil)

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## Abstract

Dielectric relaxation times over a broad range of temperature and pressure for the glass former phenolphthalein-dimethylether (PDE) reveal a change of dynamics at a characteristic relaxation time  $\tau_B$ . The value of  $\tau_B$  was found to be largely insensitive to the particular combination of pressure and temperature of the measurement. Data for a second glass former, cresolphthalein-dimethylether, having a molecular structure very close to that of PDE, were also analysed. In this case,  $\tau_B$  is much smaller, so the change of dynamics could not be observed in the elevated pressure experiments. The PDE data were in good agreement with the Adam–Gibbs model near  $T_g$  ( $\tau > \tau_B$ ), while deviating for  $\tau < \tau_B$ . Finally, a possible connection between the observed  $T_B$  and theoretical models is presented.

## 1. Introduction

The evolution of a liquid into a glass, which typically happens during cooling, is a process whose nature is still much debated. The understanding of this evolution promises a better understanding of the glassy state itself, which due to its very slow but continuous change (requiring measuring times much longer than the average lifetime of a researcher) is a very difficult problem.

In recent years much attention has been concentrated on temperatures about 20% higher than  $T_g$ , at which several phenomena have been observed [1]: breakdown of both the Stokes–Einstein relation between the viscosity and translational diffusion [2, 3] and the Debye–Stokes–Einstein relation between the viscosity and orientational relaxation [4, 5], the loss of ergodicity as predicted by mode-coupling theory (MCT) [6], a broadening of the structural relaxation

<sup>3</sup> Author to whom any correspondence should be addressed.

function [7, 8], a marked change in temperature dependence of the nanopore (unoccupied volume) radius [9], and splitting of the high-temperature relaxation into a slow process, with a relaxation time ( $\tau$ ) which diverges at  $T_g$ , and a faster relaxation, exhibiting Arrhenius behaviour through temperatures well below  $T_g$ . The change in dynamics reflected by these phenomena can be seen directly from analysis of the  $\tau$ , viscosity, or conductivity of supercooled liquids. Derivatives of these quantities exhibit a break at a temperature corresponding to that at which the aforementioned phenomena transpire [3, 10, 11].

From the theoretical point of view, the temperature,  $T_B$ , at which these phenomena occur is often interpreted as the critical temperature  $T_c$  of MCT, which in its original version [1] predicts a divergence at  $T_c$  of relaxation time and viscosity, which is not observed experimentally. This failing is ascribed to an assumed crossover from liquid-like to hopping dynamics, the latter not included in MCT. Alternatively, in the landscape model [12],  $T_B$  is regarded as the temperature at which the dynamics becomes landscape dominated [13]. In the coupling model (CM) [14], the crossover observed at  $T_B$  is interpreted as a strong increase of the degree of intermolecular cooperativity [15].  $T_B$  also recalls the (now discredited [16]) liquid–liquid transition postulated many years ago from the viscoelastic behaviour of polymers [17, 18].

While a typical experiment is done varying the temperature at atmospheric pressure, a more complete picture can be obtained when the dynamics is studied in all of pressure–temperature space [19], allowing an assessment of the influence of changes in density on the dynamics [20–24].

Herein, we describe evidence of a change of dynamics in glass formers above the glass transition for different conditions of temperature and pressure. Moreover, we show that the observed crossover is correlated with a deviation from the Adam–Gibbs (AG) model. These findings provide insight into the roles of different thermodynamic variables in the observed crossover. Finally, a possible connection between the observed crossover temperature and the critical temperature of the MCT is discussed, comparing the results for phenolphthalein-dimethylether (PDE) with previous findings for OTP.

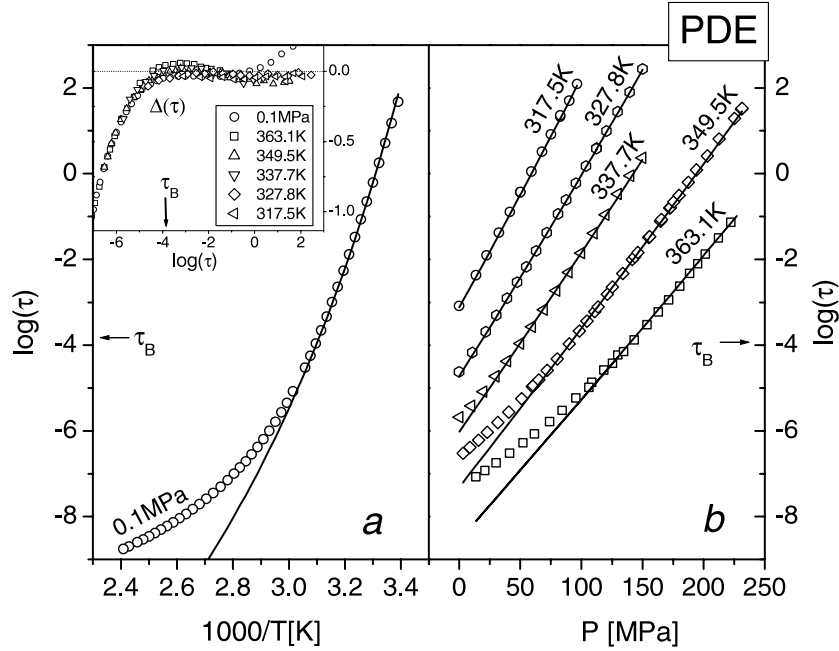
## 2. Experimental details

Dielectric spectroscopy was carried out on two glass-forming liquids, having simple molecular structures and a resistance to crystallization: PDE and cresol-phthalein-dimethylether (KDE), the latter differing from PDE by the presence of a methyl group on each phenyl ring. The sample was synthesized in the laboratory of Professor H Sillescu and obtained from Dr Roland Böhmer of Johannes Gutenberg Universität, Mainz, Germany. The glass transition temperatures of the two materials are  $T_g = 298$  K for PDE and 312 K for KDE. Spectra were acquired over ten decades of frequency, with variation of either pressure or temperature; a detailed description of the apparatus can be found elsewhere [25]. Some of the data for KDE were reported in a previous publication [26]. The samples were in the liquid state (i.e., above the pressure-dependent  $T_g$ ) during all measurements. The data for atmospheric pressure were compared with those of Stickel [27], and found to be in good agreement. Thus, we present only the latter since they have a more extended range. The relaxation time, defined from the frequency of the dielectric loss peak, corresponds approximately to the most probable relaxation time. For the materials investigated herein, no secondary relaxation was evident.

## 3. Results

### 3.1. PDE

In figure 1 we display the relaxation times for PDE versus inverse temperature (figure 1(a)) and versus pressure (figure 1(b)) at five fixed temperatures above the atmospheric pressure  $T_g$ .



**Figure 1.** Dielectric relaxation time data for PDE. (a)  $\tau$  versus inverse temperature from [34] at atmospheric pressure; (b)  $\tau$  versus pressure at fixed temperatures indicated in the plot. Solid lines are the best fit to the AG model. In the inset we show the difference  $\Delta(\tau) = \log(\tau) - \log(\tau_{AG})$  versus  $\log(\tau)$ , where  $\tau_{AG}$  is the best fit using the AG model.

A strong sensitivity of the relaxation time to both pressure and temperature is evident, making this material very suitable for this study.

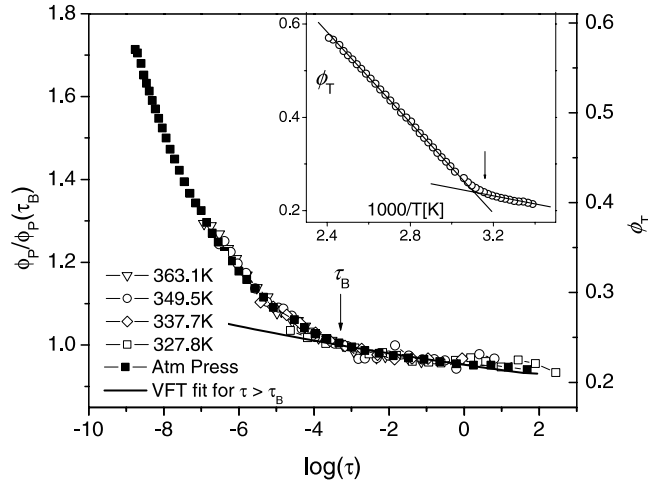
To reveal the change of dynamics at high temperature, Stickel *et al* [27] proposed the use of the function  $\phi_T = (d(\log(\tau))/d(1000/T))^{-\frac{1}{2}}$ . Vogel–Fulcher (VF) behaviour is often observed near  $T_g$  [28, 29]:

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

where  $T_0$  is the Vogel temperature,  $D$  is the fragility parameter, and  $\tau_0$  is the relaxation time in the limit of high temperatures. The function  $\phi_T$  is very useful for evidencing deviation from this behaviour because it transforms a VF into a linear dependence with respect to inverse temperature. From calculating  $\phi_T$  for PDE, we determined a change of slope at  $\tau_B \sim 10^{-4}$  s [30]. We consider that the pressure behaviour of  $\tau$  in the proximity of the glass transition can be well described by a VF-like equation [31, 32]:

$$\tau(P) = \tau_P \exp\left(\frac{D_P P}{P_0 - P}\right), \quad (2)$$

where  $P$  is the pressure,  $\tau_P$  can be obtained from isobaric data at atmospheric pressure,  $P_0$  denotes the pressure at which  $\tau$  diverges, and  $D_P$  can be referred to, for consistency, as the pressure fragility parameter [33]. Consequently, a function similar to  $\phi_T$  can be defined:  $\phi_P = (d(\log(\tau))/dP)^{-\frac{1}{2}}$ . The function  $\phi_P$  is calculated for the four isotherms. At higher temperature there is a clear change in the pressure dependence [30]. The value of the relaxation time corresponding to this change is  $\tau_B \sim 10^{-4}$  s, equivalent to the value at atmospheric pressure [34]; that is,  $\tau_B$  is independent of temperature and pressure.



**Figure 2.**  $\phi_P$  calculated for the four isotherms (figure 1(a)) normalized by their value at  $\tau_B$ , together with  $\phi_T$ , with all functions plotted versus  $\log(\tau)$ . In the same figure, to evidence the deviation from a VF, we report also the  $\phi_T$  calculated for the VF fit (valid for  $\tau > \tau_B$ ). In the inset we show  $\phi_T$  versus inverse temperature.

As further evidence that the pressure crossover has the same characteristic time as its temperature counterpart  $\phi_T$ , we plot in figure 2 both functions  $\log(\tau)$ . In this figure we show the function  $\phi_P$  calculated for the four isotherms at higher temperatures normalized by their value at  $\tau_B$ , together with  $\phi_T$ . Note that in the plots of  $\phi_T$  and  $\phi_P$  versus  $\log(\tau)$ , the VF behaviour is no longer linear; thus to evidence the deviation from a VF form, the  $\phi_T$  calculated for the VF fit (valid for  $\tau > \tau_B$ ) is also displayed. It is evident that the behaviour of the function  $\phi_P$  is the same, and coincides with that of the Stickel function  $\phi_T$ .

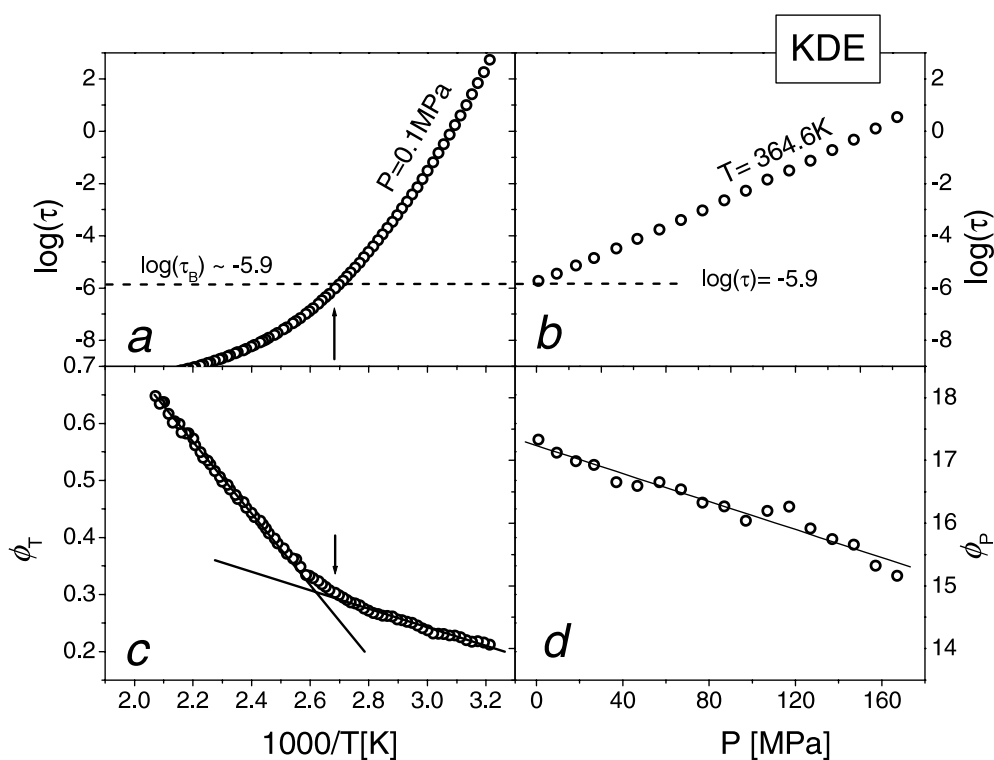
### 3.2. KDE

The dielectric relaxation times for KDE for varying temperatures at atmospheric pressure and varying pressures at  $T = 364.6$  K are shown in figures 3(a) and (b) respectively. Like PDE, KDE has a strong pressure and temperature dependence. Comparing the pressure dependence of the glass transition temperature  $dT_g/dP$  (calculated at atmospheric pressure) and the steepness index  $m = \left. \frac{d \log(\tau)}{d(T/T_g)} \right|_{T=T_g}$ , we have for KDE  $dT_g/dP = 307$  K GPa $^{-1}$  and  $m = 72.5$  [26] and for PDE  $dT_g/dP = 260$  K GPa $^{-1}$  and  $m = 85$ . Thus, KDE is more sensitive to pressure but less sensitive to temperature. This difference may seem surprising considering that their molecular structures are very close. However, the activation volume,  $\Delta V (= RT \frac{\partial \log \tau}{\partial P})$  at  $T_g$ , which is proportional to the product of  $m$  and  $dT_g/dP$  [32]:

$$\Delta V(T_g) = \ln(10) R m \frac{dT_g}{dP} \quad (3)$$

where  $R$  is the gas constant, is equal to 420 cm $^3$  mol $^{-1}$  for both PDE and KDE. The similarity of their molecular structures is reflected in  $\Delta V$ .

In figures 3(c) and (d) we display the functions  $\phi_T(T)$  and  $\phi_P(P)$  as calculated from the  $\tau(T, P)$  data for KDE. From the  $\phi_T$  behaviour it is evident that a change in the dynamics occurs at  $\tau_B \sim 10^{-6}$  s, which is about a hundredfold smaller than  $\tau_B$  for PDE. Our value of  $\tau_B$  is lower than that reported in [26]. The data are the same, and the difference is due only to the



**Figure 3.** Dielectric relaxation time data for KDE: (a)  $\tau$  versus inverse temperature from [34] at atmospheric pressure; (b)  $\tau$  versus pressure at fixed temperature indicated in the plot; (c) the derivative function  $\phi_T$  versus inverse temperature for data reported in (a); (d) the derivative function  $\phi_P$  versus pressure for the data reported in (b).

different method used to determine  $T_B$ . No change in the slope of  $\phi_P(P)$  is observed, since the pressure measurements cover only a limited range. This result is at least consistent with a constant  $\tau_B(T, P)$ . This comparison of KDE and PDE emphasizes that the value of  $\tau_B(T, P)$  is not universal. It is striking that for materials having very similar molecular structures,  $\tau_B$  differs by about two orders of magnitude.

## 4. Discussion

### 4.1. Test of the AG model

Of the different theoretical models proposed for interpreting the slowing down of the dynamics upon approach to the glass transition, much attention has been directed to the model of AG [35], which predicts

$$\tau = \tau_{AG} \exp\left(\frac{A}{TS_c}\right) \quad (4)$$

where  $S_c$  is the configurational entropy,  $A$  is a constant related to the intermolecular potential, and  $\tau_{AG}$  is the relaxation time in the limit of high temperatures. The important result of this model is establishing a link between the dynamics ( $\tau$ ) and thermodynamical quantities ( $S_c$ ). It is noteworthy that equation (4) has been found to be valid for simulations at short times [36, 37], which arise from a theoretical approach different to that used originally by AG.

The operative definition proposed by AG for determining  $S_c$  is considering it as equal to the excess entropy,  $S_{ex}$ , of the melt with respect to the crystal. However, as pointed out by Goldstein [38], this definition is problematic, because  $S_{ex}$  may include vibrational terms, with consequent overestimation of  $S_c$ . This point has recently been emphasized by Johari [39, 40] and Angell [41]. Nevertheless, tests of the AG model using  $S_{ex}$  have been successful for temperatures not too far from  $T_g$  [42–45], presumably reflecting at least proportionality between  $S_c$  and  $S_{ex}$  [41, 46], as found by computer simulations [47, 48].

Taking  $S_c$  equal to  $S_{ex}$ , the full pressure and temperature dependences can be written as

$$S_c(T, P) = \Delta S_{fus} + \int_{T_K}^T \frac{\Delta C_P(T')}{T'} dT' - \int_0^P \Delta \left( \frac{\partial V}{\partial T} \right)_{P'} dP' \quad (5)$$

where  $\Delta S_{fus}$  is the entropy of fusion. The first integral is related to the excess molar heat capacity,  $\Delta C_P = C_P^{melt} - C_P^{crystal}$ , of the melt relative to the crystal, and the second integral can be expressed in terms of the excess molar thermal expansion,  $\Delta \left( \frac{\partial V}{\partial T} \right)_P = \left( \frac{\partial (V^{melt} - V^{crystal})}{\partial T} \right)_P$ . At atmospheric pressure ( $P \sim 0$ ), the second integral is zero, and since the temperature dependence of the excess heat capacity can be described over a limited range by  $\Delta C_P(T) = \kappa/T$ , then  $S_c(T) = S_\infty - \kappa/T$ , where  $\kappa$  is a constant and  $S_\infty$  is the limit of  $S_c$  at very high temperatures [45]. On substituting this equation into equation (4), the VF expression is obtained, where  $T_0$  is the Vogel temperature ( $T_0 = \kappa/S_\infty$ ) and  $D$  ( $D = C/\kappa$ ) is the fragility parameter. At pressures above atmospheric, the second integral of equation (5), describing the isothermal reduction of  $S_c$ , is non-negligible. On substituting equation (5) in (4), a VF-like equation for  $\tau(T, P)$  is again obtained, with the Vogel temperature now defined as [49]

$$T_0^*(T, P) = \frac{T_0}{1 - \frac{1}{S_\infty} \int_0^P \Delta \left( \frac{\partial V}{\partial T} \right)_{P'} dP'} \quad (6)$$

At low pressures, the pressure dependence of the crystal thermal expansivity is negligible [49], and equation (6) can be rewritten as

$$T_0^*(T, P) = \frac{T_0}{1 + \frac{1}{S_\infty} \left[ P \left( \frac{\partial V}{\partial T} \right)_{P=P_{atm}}^{cryst} - \int_0^P \left( \frac{\partial V}{\partial T} \right)_{P'}^{melt} dP' \right]} \quad (7)$$

in which the integral can be calculated if  $V(T, P)$  for the melt is known. Accordingly, a function describing both the pressure and temperature dependence of  $\tau$  according to equation (4) will require, together with the three VF parameters  $D$ ,  $T_0$ , and  $\tau_0$  for  $P \sim 0$ , two additional quantities  $S_\infty$  and  $\left( \frac{\partial V}{\partial T} \right)_{P=P_{atm}}^{cryst}$ . In favourable cases, these can be related to macroscopic physical properties of the material. Tests of the AG model have been previously carried out, using approximate values for  $\left( \frac{\partial \Delta V}{\partial T} \right)_P$  [25, 49–51]. Herein, we execute a more accurate assessment, by calculating the integral of the thermal expansivity of the melt from  $V(T, P)$  data [1, 51] for each condition of temperature and pressure.

The fit to equations (4) and (5) was carried out on both isobaric (one pressure) and isothermal (five temperatures) data. The analysis was limited to  $\tau_B \sim \tau < 10^{-4}$  s because of the deviation from a single VF form evidenced from the Stickel plot (inset, figure 2). For  $\tau < \tau_B$  in figure 1, a good agreement of the fit (solid lines) to the experimental data for all temperatures and pressures is evident. The best-fit parameters were  $\log(\tau_0) = -20.7$ ,  $D = 19.2$ ,  $T_0 = 215$  K,  $S_\infty = 112$  J K<sup>-1</sup> mol<sup>-1</sup>, and  $\left( \frac{\partial V}{\partial T} \right)_{P=P_{atm}}^{cryst} = 1.7 \times 10^{-4}$  cm<sup>-3</sup> K<sup>-1</sup>. The first three values are equal to those found previously for atmospheric pressure [34, 52]. The thermal expansivity obtained for the crystal is quite close to the value measured at  $P = 10$  MPa, namely  $\left( \frac{\partial V}{\partial T} \right)_{P=10 \text{ MPa}}^{cryst} = 1.9 \times 10^{-4}$  cm<sup>-3</sup> K<sup>-1</sup> [51].

It is interesting that the best fits to the AG model (solid lines in figure 1(b)), which are nearly linear, show a clear deviation for short  $\tau$ , similar to the deviation in the  $\tau$  versus

**Table 1.** The expansion coefficient  $\alpha$  and isothermal compressibility  $\beta$  for PDE at the  $T$  and  $P$  at which the change of dynamics is observed, and the calculated value of the expression in equation (8).

$T$ (K)	$P$ (MPa)	$\alpha \times 10^4$ (K $^{-1}$ )	$\beta \times 10^4$ (MPa $^{-1}$ )	$T_c \left( \frac{\beta}{dT/dP _{\tau=\tau_c}} - \alpha \right)$
318.9	0.1	6.2	4.0	0.26
327.8	30.4	5.8	3.7	0.25
337.7	66.2	5.4	3.4	0.23
349.5	108.5	5.0	3.0	0.21
363.1	160.7	4.7	2.7	0.19

temperature plot. To show this better, we plotted, in the inset to figure 1, the difference between the experimental points and the best fit to the AG model ( $\Delta(\tau) = \log(\tau) - \log(\tau_{AG})$ ). The deviation for all data (both isobaric and isothermal) occurs at about the same relaxation time. This result recalls the deviations from the AG model observed for several materials from measurements at atmospheric pressure, in which  $S_c$  was calculated from calorimetric data [45, 53].

#### 4.2. Comparison with other theoretical predictions

It is significant that the changes in dynamics shown herein have similarities to the behaviour reported for other glass formers, for example, ortho-terphenyl (OTP) [54]. In a recent review on OTP [55], Tölle showed that the temperature for the change in dynamics as determined using the Stickel function,  $T_B \cong 290$  K at  $\tau_B \sim 10^{-6}$  s [54], is very close to the critical temperature,  $T_c$ , of MCT [6]. More relevant, Tölle *et al* concluded, from measurements of the pressure and temperature dependence of the static structure factor [19, 55], that the structure factor does not change significantly along an isochronous line. This implies that the relaxation time at the dynamic singularity of MCT should be independent of pressure and temperature, analogous to the results herein for  $\tau_B$ . However, the  $T_c$  of MCT corresponds to a transition that is not observed in relaxation data, and it remains to be established whether this can be identified with  $T_B$ .

To compare our results with the findings of Tölle for OTP, we verified the relationship that he proposed [55]:

$$T_c \left( \frac{\beta}{dT/dP|_{\tau=\tau_c}} - \alpha \right) \cong \frac{1}{4} \quad (8)$$

from MCT, which predicts and expresses the repulsive part of the potential. In equation (8),  $\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$  is the isothermal compressibility and  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$  is the thermal expansion coefficient. Considering  $T_c = T_B$  and  $\tau_c = \tau_B$ , we calculate the values of  $\alpha$  and  $\beta$  from  $V(T, P)$  measurements on PDE [51], together with the value of the expression in equation (8). The results, reported in table 1, are very close to the expected values. The deviation from the predicted value of 0.25 is of the order observed by Tölle for OTP [55]:  $0.23 \pm 0.03$  for PDE versus  $0.26 \pm 0.03$  for OTP [55].

In the framework of the CM [14], the constancy of  $\tau_B$  is consistent with the observed constancy of the shape of the dielectric relaxation spectra at the same relaxation time for different conditions of  $T$  and  $P$  [25, 26]. Thus, the expected correlation of the crossover with the strong increase in the severity of intermolecular cooperativity is borne out by the results herein.



## 5. Conclusions

Evidence of a change of dynamics in PDE under different conditions of temperature and pressure is reported. We observe that for very different values of  $T$  and  $P$ , the change of dynamics transpires at the same relaxation time,  $\tau_B \sim 10^{-4}$  s. To show this more clearly, we make use of the Stickel function  $\phi_T$  and of its pressure counterpart  $\phi_P$  to obtain the master curves in figure 2. It is worth noting that we observed the same behaviour, with  $\tau_B(T, P) = \text{constant}$ , for two other materials, and in these cases also,  $\tau_B$  was found to be dependent on the material [25, 30].

Data for a second glass former (KDE) having a molecular structure very similar to that of PDE were also analysed. In this case,  $\tau_B$  is much smaller, so the change of dynamics could not be observed in the elevated pressure experiments. Evidently,  $\tau_B$ , while constant for a given chemical species, is not universal.

An analysis of PDE data using the AG model was carried out taking into account the  $V(T, P)$  dependence. The model was found to describe accurately the  $\tau$ -behaviour in the proximity of  $T_g$  for  $\tau > \tau_B$ , while a deviation from the AG prediction is observed in both the temperature and pressure data for  $\tau < \tau_B$ .

Finally, a possible connection between the observed  $T_B$  and the critical temperature of the MCT is discussed. The results for PDE are compared with previous findings for OTP.

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