

Pressure dependence of structural relaxation time in terms of the Adam-Gibbs model

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A new equation describing the behavior of the structural relaxation time, $\tau(T,P)$, as a function of both pressure and temperature, is discussed. This equation has been derived from the Adam-Gibbs theory by writing the configurational entropy, S_c , in terms of the excess thermal heat capacity and of the molar thermal expansion. Consequently, the parameters introduced in the expression are directly related to specific physical properties of the material, such as the thermal expansion coefficient α and the isothermal bulk modulus K_0 . At a fixed pressure, for low pressures, the found equation reduces to a Vogel-Fulcher-Tammann equation of τ versus temperature with the fragility parameter independent from pressure. The equation for $\tau(T,P)$ was successfully tested directly by fitting the dielectric relaxation time data for two isothermal and one isobaric measurements on diglycidyl ether of bisphenol-A, carried out in previous experiments. The parameters estimated by the best fit were in reasonable agreement with the values determined from the known physical properties of the material. Finally, the expression for the change versus pressure of the temperatures at which the same value of τ_{\max} is obtained (e.g., the change versus pressure of the glass transition temperature) agrees with several expressions previously proposed in the literature to provide a phenomenological description of the observed phenomena.

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I. INTRODUCTION

By cooling at a sufficiently high rate, almost every liquid can be turned into a glass, i.e., an amorphous “phase” in which the molecular motions are almost frozen, and which has been conventionally defined by values of the structural relaxation time higher than 10^2 s and of viscosity exceeding 10^{13} P [1]. In a similar way, the glass transition can be approached by applying a sufficiently high pressure to a liquid. In fact, the increase of pressure, like the decrease of temperature, has the effect of slowing down the molecular motion. These two different ways of approaching the glass transition have several similar features, which can give interesting hints for the understanding of the glass transition phenomenon.

Probably, the more important signature of the glass transition is the strong increase of the structural relaxation time (or viscosity) that in a relatively small range of temperature may vary of more than ten orders of magnitude. The temperature dependence of the structural relaxation time τ , for most of the glass-forming liquids, can be described over a wide dynamical range by the empirical Vogel-Fulcher-Tammann (VFT) equation [2]

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

where τ_0 is the relaxation time at very high temperatures, D is the fragility parameter, T is the absolute temperature, and

T_0 the Vogel temperature. The fragility parameter accounts for the departure of $\tau(T)$ from the Arrhenius behavior and is widely used in classifying the glass-forming liquids as strong (high D) and fragile (low D) [3].

Recently Richert and Angell [4] have shown that the temperature behavior of τ as expressed by Eq. (1) is in good agreement with the Adam-Gibbs (AG) theory [5] which is based on the concept of configurational entropy earlier discussed by the theory of Gibbs-DiMarzio [6]. An extension of this last theory to incorporate the effect of pressure was also developed [7], although it does not provide an explicit pressure dependent function for the relaxation time. So far, the search for an appropriate description of the structural relaxation time with pressure has been still partially entrusted to a phenomenological approach.

In this work, starting from the original picture of the AG theory, we tried to give a physical explanation and a description of the behavior of the structural relaxation time observed by varying the pressure.

II. THEORY

A. Pressure and temperature dependence of the configurational entropy

The AG theory is based on the assumption of a cooperatively rearranging regions. The theory [5] gives an expression for the relaxation time that contains the configurational entropy (S_c)

$$\tau = \tau_0 \exp\left(\frac{C_{AG}\Delta\mu}{TS_c}\right), \quad (2)$$

where $\Delta\mu$ is the free energy barrier (per molecule in the

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cooperative region) to rearrangements, C_{AG} is a constant, and $S_c(T)$ is defined as the excess entropy, $S_c(T) = S^{\text{melt}} - S^{\text{crystal}}$, and measures all the entropy of the melt apart for the vibrational contributions. Approaching the glass transition by changing the temperature, the departure from Arrhenius behavior comes from the temperature dependence of $S_c(T)$, which depends on the value of the configurational heat capacity, ΔC_p . The initial form of this model [5] was found to have some limits, which can be overcome by further extensions to the initial model proposed by Ngai [8]. Notwithstanding its limits, the AG theory through the link between τ and S_c , as expressed by Eq. (2), is able to give an elegant explanation of the change of the $\tau(T)$ on approaching the glass transition.

Recently, Richert and Angell [4] directly compared the behavior of the dielectric relaxation time $\tau(T)$ with the experimental data of the configurational entropy, $S_c(T)$, for several glass-formers and found that Eq. (2) is in good agreement with experimental data in the range $T_g < T < T_B$, where T_B is the temperature below which the VFT equation applies and at which a qualitative change of the behavior of $\tau(T)$ is observed [9]. $S_c(T)$ was estimated as [4]

$$S_c(T) = \int_{T_K}^T \frac{\Delta C_p(T')}{T'} dT', \quad (3)$$

where $\Delta C_p = C_p^{\text{melt}} - C_p^{\text{crystal}}$ is the excess heat capacity and T_K is the Kauzmann temperature.

For a number of glass formers the excess heat capacity was documented before to vary inversely with absolute temperature $\Delta C_p = K/T$, where K is a constant [4,10,11]. From which

$$S_c(T) = \int_{T_K}^T \frac{K}{T'^2} dT' = \frac{K}{T_K} - \frac{K}{T} = S_\infty - \frac{K}{T}, \quad (4)$$

this expression of $S_c(T)$ substituted in Eq. (2) is consistent with a VFT behavior.

A further check of the validity of the AG model [Eq. (2)] in describing the data varying the pressure (still above the glass transition), could be done by knowing the dependence of the configurational entropy on both temperature and pressure, $S_c(T,P)$. The pressure dependence of S_c can be obtained by adding to Eq. (3) the term related to the molar thermal expansion

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

where

$$\Delta \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial V}{\partial T} \right)_P^{\text{melt}} - \left(\frac{\partial V}{\partial T} \right)_P^{\text{crystal}}$$

is the difference of the molar thermal expansivity of the melt and the crystal. The dependence of the volume on the pressure can be estimated by using the Tait equation, found to be valid for a wide range of materials including liquids and polymers, for changes of the volume, $V(T,P)$, up to 40% of the initial value, $V(T,0)$ [12,13]

$$V(T,P) = V(T,0) [1 - C \ln(1 + P/B(T))], \quad (6)$$

where C is a dimensionless constant and $B(T)$ is a temperature dependent factor with the same dimension as pressure. The value of C was shown to be almost constant for a wide range of materials (best average value $C = 0.0894$) and the temperature dependent factor can be expressed by $B(T) = b_1 \exp(-b_2 T)$ [14] (where for liquids $b_1 \sim 300$ MPa and $b_2 \sim 4 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ [12]).

By using Eq. (6) and the expression of $B(T)$ by Simha, Wilson, and Olabisi [14] it follows that

$$\begin{aligned} \left(\frac{\partial V^{\text{melt}}}{\partial T} \right)_P &= \left(\frac{\partial V^{\text{melt}}}{\partial T} \right)_{P=0} \left[1 - C \ln \left(1 + \frac{P}{B(T)} \right) \right] \\ &\quad - V^{\text{melt}}(T,0) C \frac{b_2}{1 + [P/B(T)]} \frac{P}{B(T)}. \end{aligned} \quad (7)$$

Regarding the variation with pressure of the molar thermal expansivity for the crystal, we considered it as negligible with respect to that of the melt so that it was assumed $(\partial V^{\text{crystal}}/\partial T)_P = (\partial V^{\text{crystal}}/\partial T)_{P=0}$. Therefore by substituting Eq. (7) in Eq. (5), solving the integrals, and using Eq. (4) we found the following expression for $S_c(T,P)$

$$\begin{aligned} S_c(T,P) &= S_\infty - \frac{K(P)}{T} + \delta \left\{ -(\beta + \gamma - 1)P + (\gamma - 1)B(T) \right. \\ &\quad \left. \times \ln \left(1 + \frac{P}{B(T)} \right) + \gamma P \ln \left(1 + \frac{P}{B(T)} \right) \right\}, \end{aligned} \quad (8)$$

where β , γ , and δ are, respectively,

$$\beta = \frac{1}{b_2 C V^{\text{melt}}(T,0)} \Delta \left(\frac{\partial V}{\partial T} \right)_{P=0}; \quad \gamma = \frac{\alpha}{b_2};$$

$$\delta = C V^{\text{melt}}(T,0) b_2$$

and $\alpha = 1/V(\partial V/\partial T)_P$ is the coefficient of thermal expansion of the melt.

By substituting Eq. (8) in Eq. (2) we found the following expression for $\tau(T,P)$

$$\tau(T,P) = \tau_0 \exp \left\{ \frac{C_{AG} \Delta \mu}{T [S_\infty - (K/T) + \delta \{ -(\beta + \gamma - 1)P + (\gamma - 1)B(T) \ln(1 + [P/B(T)]) + \gamma P \ln(1 + [P/B(T)]) \}]} \right\}. \quad (9)$$

This expression can be written in a VFT-like [Eq. (1)] form with

$$T_0(P) = \frac{T_0(P=0)}{[1 + (\delta/S_\infty)\{-(\beta + \gamma - 1)P - (1 - \gamma)B(T)\ln(1 + [P/B(T)])\} + \gamma P \ln(1 + [P/B(T)])]}, \quad (10)$$

$$D = \frac{C_{AG}\Delta\mu}{K},$$

where $T_0(P=0) = K/S_\infty$.

From Eq. (10) it is evident that for an isobaric measurement at high pressure, the dependence of B , β , γ , and δ on temperature could give a deviation of $\tau(T, P = \text{const})$ from a VFT behavior. However, the dependence of these parameters on the temperature is known to be very weak so that the deviation from VFT behavior should be observable only at high pressure ($P \gg B$). On the other hand, if the dependence on the temperature of these parameters is negligible, a VFT equation with the same fragility parameter D should provide a good description of the isobaric measurements.

Regarding the isothermal measurements, a dependence on the pressure of ΔC_p could limit the validity of Eq. (10). The experimental measurements of ΔC_p versus pressure reported in the literature show a very weak dependence of ΔC_p on the pressure that is therefore negligible in Eq. (10) [15].

III. COMPARISON WITH EXPERIMENTAL RESULTS

As discussed above and from Eq. (10), the independence of the fragility parameter D from the pressure follows. This prediction agrees well with the results of several experiments undertaken in isobaric conditions on methanol [16], orthoterphenyl (OTP) [17], dibutyl-phthalate [18], and epoxy resins [19–21] which found a value of D that, within the experimental errors, does not depend on pressure.

Moreover, as a correlation between the fragility parameter and the shape of the main relaxation was found in a large number of glass-formers [22], the change of fragility in isothermal conditions can be observed by the change of the shape of the structural relaxation (i.e., change of the shape parameters) for isocronal spectra (i.e., having the same τ_{max}). On this basis, the independence of the fragility parameter D from the pressure was also verified in isothermal measurements on polypropylene glycol (PPG) [23] and epoxy resins [21,24].

To directly test Eq. (9) we analyzed data of $\tau(T, P)$ for diglycidyl ether of bisphenol-A (DGEBA), previously reported [24,25]. The measurements on the glass-former DGEBA were carried out by wideband dielectric spectroscopy over a wide range of frequencies, by varying either temperature (in isobaric conditions, $P = 0.1$ MPa, atmospheric pressure) or pressure (in two isothermal conditions, $T = 293$ and 313.85 K) down to temperature-induced and pressure-induced glass transition. At atmospheric pressure, DGEBA is a fragile glass-former in which a significant change of the structural relaxation time can be induced under compression with moderate changes of pressure. Thanks to this characteristic, the isothermal and isobaric measurements of the structural relaxation time of DGEBA were accurate over a wide dynamical range, thus allowing an accurate test of Eq. (9).

To better separate in Eq. (9) the part dependent on the pressure from that on the temperature, we rewrite it as

$$\tau(T, P) = \tau_0 \exp\left\{\frac{A}{T - T_0^* + T(\delta/S_\infty)\{-(\beta + \gamma - 1)P + (\gamma - 1)B(T)\ln(1 + [P/B(T)])\} + \gamma P \ln(1 + [P/B(T)])}\right\}, \quad (11)$$

where $T_0^* = T_0(P=0)$ and $A = D_0^*$.

In this way, the parameters A , T_0^* , and τ_0 can be estimated by the best fit of the isobaric measurement at atmospheric pressure (we considered $P = 0.1$ MPa ~ 0 pressure), while the other parameters (δ/S_∞ , β , γ , and B) can be estimated by the best fit of the isothermal measurements keeping the other parameters constant.

The behavior of the structural relaxation time τ at atmospheric pressure versus the reciprocal temperature is shown in Fig. 1. The relaxation time was estimated as $\tau = 1/(2\pi f_{\text{max}})$, where f_{max} is the frequency of the maximum loss of the main relaxation. Isobaric (atmospheric pressure) conductivity data are also available; the conductivity was proved [26] to be coupled to τ according to the hydrodynamic Debye-Stokes-Einstein relation, $\sigma \propto \tau^{-1}$. Over the

temperature range, 266–343 K, τ showed a change over 10 decades, which can be well-described by a VFT behavior as shown by the solid line in Fig. 1. Conductivity data (open circle in Fig. 1), shifted on the logarithmic scale to match the dielectric relaxation time, were also considered within the temperature range of the dielectric measurements in order to improve the information at high temperature. A change of dynamics at the temperature, $T_B = 352$ K, was previously reported [24], but here, considering only temperatures $T < T_B$, it is not important for the following discussion. The fit parameters estimated by using Eq. (11) for $P = 0$ (i.e., a VFT equation) are reported in Table I.

The pressure dependence of the structural relaxation for the two isothermal measurements at $T = 293$ and 313.85 K are shown in Figs. 2 and 3 (open circles), respectively.

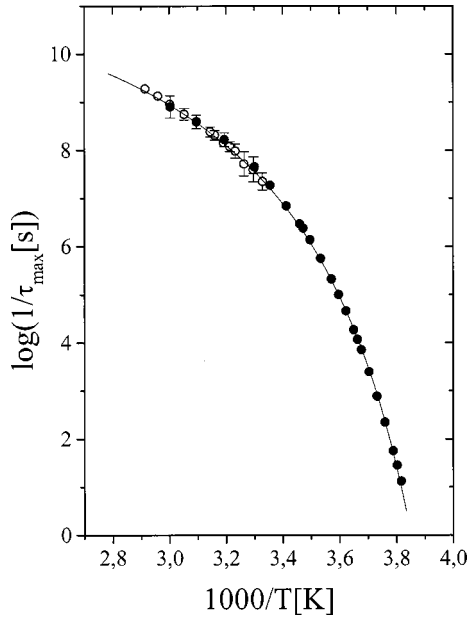


FIG. 1. Structural relaxation time data, $\log_{10}(1/\tau_{\max}[\text{s}])$, obtained from dielectric relaxation (solid circles) and dc conductivity (open circles), at ambient pressure vs temperature. When not reported error bars are smaller than the symbol size. The solid line is the best fit obtained by using Eq. (11) for $P=0$, i.e., with a VFT equation, the parameters are shown in Table I.

In principle, the free parameters necessary to fit the pressure behavior of τ by using Eq. (11) are at least four and this large number could raise some doubts on the validity of our test. Therefore we decided to fix at an estimate value two of these parameters (B and γ), leaving free only two parameters (β and δ/S_{∞}).

In fact, the parameter B can be determined from the value of the isothermal bulk modulus, K_0 , by using the relationship $B=K_0C$ [13]. For DGEBA we could use the value of $K_0=2.9$ GPa valued previously at $T=293$ K [27] while, not having the specific value of C , we used the value of $C=8.94 \times 10^{-2}$ which is a reasonable estimate for many liquids and polymers [12,14]. Using this value for K_0 and C we found $B=260$ MPa. As discussed before, the value of B is expected to change by varying the temperature, and for the two temperatures considered the values of B should differ by a few percent; the value of B was already approximated, so this further correction was neglected.

TABLE I. Best-fit parameters obtained by using Eq. (11) to fit the structural relaxation time of DGEBA for an isobaric measurement (ambient pressure $P=0$) and two isothermal measurements ($T=273$ and 313.85 K, respectively).

Pressure and temperature range	A [K]	T_0^* [K]	$\log(1/\tau_0)$	β	γ	δ/S_{∞} [MPa $^{-1}$]	B [MPa]
$P=0$; $T=266-343$ K	725 ± 6	233.6 ± 0.2	12.13 ± 0.02				
$P=0-235$ MPa $T=293$ K	721	233.6	12.14	(1.04 ± 0.01)	0.12	$(7.0 \pm 0.1) \times 10^{-4}$	260
$P=0-339$ MPa $T=313.85$ K	721	233.6	12.14	(1.13 ± 0.01)	0.12	$(6.6 \pm 0.1) \times 10^{-4}$	260

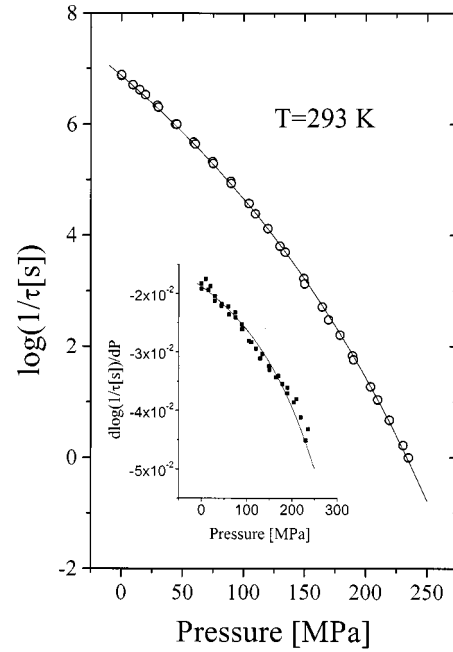


FIG. 2. Structural relaxation time data, $\log_{10}(1/\tau[\text{s}])$, obtained from dielectric relaxation (open circles) at $T=293$ K vs pressure. When not reported the error bars are within the experimental symbol size. The solid line is the best fit obtained by using Eq. (11) by using as free parameters β and δ/S_{∞} , while the other parameters (A , T_0^* , τ_0 , B , and γ) were fixed as discussed in the text. The values of all the parameters are shown in Table I. Shown in the inset is the derivative respect to the pressure of the experimental data (solid squares) and of the fitting function (solid line).

On the other hand, the parameter γ was estimated as $\gamma = \alpha/b_2 = 0.12$, considering the known thermal expansion coefficient α of DGEBA ($\alpha = 4.87 \times 10^{-4} \text{ K}^{-1}$ [27]) and the typical value of the parameter b_2 for liquids and polymers elsewhere reported ($b_2 = 4 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ [12,14]).

Moreover, the values of A , T_0^* , and τ_0 were adjusted within the estimated error (provided by the best fit of the isobaric measurement) so that the value of Eq. (11) for $P=0$ actually coincided with the data at $P=0$ of the isothermal measurements.

In conclusion, the expected behavior was checked by using Eq. (11) with β and δ/S_{∞} as free parameters, while B , γ , A , T_0^* , and τ_0 were fixed at the estimated values.

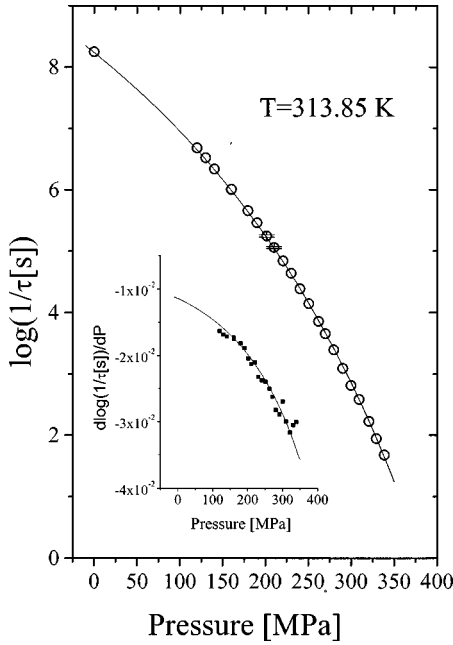


FIG. 3. Structural relaxation time data, $\log_{10}(1/\tau[\text{s}])$, obtained from dielectric relaxation (open circles) at $T=313.85$ K vs pressure. When not reported the error bars are within the experimental symbol size. The solid lines are the best fit obtained by using Eq. (11) by using as free parameters β and δ/S_∞ , while the other parameters (A , T_0^* , τ_0 , B , and γ) were fixed as discussed in the text. The values of all the parameters are shown in Table I. Shown in the inset is the derivative respect to the pressure of the experimental data (solid squares) and of the fitting function (solid line).

The best fits obtained in this way are shown in Figs. 2 and 3 (solid lines), while the parameters are in Table I. To show the good agreement of the data with the best fit, in the inset of Figs. 2 and 3 also shown are the derivatives with respect to P of the data (solid squares) and of the fitting curves (solid line).

The resulting best fit parameters are just of the correct order of magnitude and from them reasonable values for S_∞ and $\Delta(\partial V/\partial T)_P$ can be estimated. In fact, from the values $\delta/S_\infty = (6.6 \pm 0.1) \times 10^{-4} \text{ MPa}^{-1}$ and $\delta/S_\infty = (7.0 \pm 0.1) \times 10^{-4} \text{ MPa}^{-1}$ we estimated [by using $C=0.0894$, $V^{\text{melt}}(T,0) = 3.2 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$ and $b_2 = 4 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$] $S_\infty = 173 \pm 3$ and $163 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. These values of S_∞ are very close to those estimated for others glass-formers [4]. Moreover, from the best fits of the isothermal measurements at $T=293$ and 313.85 K we estimated $\Delta(\partial V/\partial T)_P = (1.19 \pm 0.01) \times 10^{-7}$ and $(1.29 \pm 0.01) \times 10^{-7} \text{ m}^3 \text{ K}^{-1} \text{ mol}^{-1}$, respectively, and also these values are very reasonable considering that for DGEBA, $(\partial V^{\text{melt}}/\partial T)_P = \alpha V^{\text{melt}}(T,0) = 1.6 \times 10^{-7} \text{ m}^3 \text{ K}^{-1} \text{ mol}^{-1}$. In slight disagreement with our expectations are the differences found between the values of the parameters β and δ/S_∞ estimated at two different temperatures, which are larger than the estimated errors. On the other hand, we noticed that their product is indeed independent from the temperature ($\beta\delta/S_\infty = 7.3 \pm 0.2 \text{ MPa}^{-1}$ at $T=293$ K and $\beta\delta/S_\infty = 7.4 \pm 0.2 \text{ MPa}^{-1}$ at $T=313.85$ K).

Moreover, by using Eq. (10) with the parameters esti-

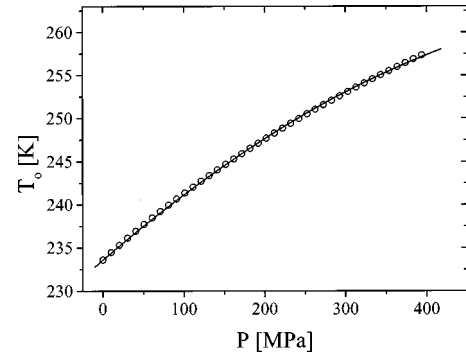


FIG. 4. $T_0(P)$ estimated (open circles) by using Eq. (10) with the parameters $T_0^* = 233.6$ K, $\beta = 1.04$, and $\delta/S_\infty = 7.0 \times 10^{-4} \text{ MPa}^{-1}$ estimated by the best fit of the isothermal measurement at $T=293$ K and the parameters estimated from the literature $B=260$ MPa and $\gamma=0.12$. The solid line is the best fit to the data obtained by using a second order polynomial equation $T_0(P) = T_0^* + aP + bP^2$, with $T_0^* = 233.6$ K (fixed) and the estimated parameters were $a = (81.1 \pm 0.2) \times 10^{-3} \text{ MPa}^{-1} \text{ K}$ $b = (-54.1 \pm 0.7) \times 10^{-6} \text{ MPa}^{-2} \text{ K}$.

mated by the best fit, it is possible to plot the expected $T_0(P)$ as shown in Fig. 4. The behavior shows a clear deviation from a simple linear dependence of T_0 on the pressure for high enough pressure. It is important to notice that the pressure behavior given by Eq. (10) (except for an additive constant) not only describes $T_0(P)$ but also the behavior of the temperature (at a fixed pressure) corresponding to the same value of τ_{max} [e.g., $T_g(P)$].

This behavior is in agreement with results found in previous investigations in which a clear deviation from a linear dependence was reported [17,21,23,24,28]. In particular Schug, King, Jr., and Böhmer for OTP and salol [17], Andersson and Andersson for PPG [23], Corezzi *et al.* for DGEBA [24], and Paluch, Hensel-Bielówka, and Ziolo for poly[(phenyl glycidyl ether)-co-formaldehyde] [21] found that this nonlinear behavior can be well-described by a second order polynomial function, which was only derived on a phenomenological approach.

In Fig. 4 the solid line is the best fit using a second order polynomial, $T_0(P) = T_0^* + aP + bP^2$, to the $T_0(P)$ estimated by Eq. (10), the very good agreement between the two behaviors is clear. Therefore our result seems able to also give a satisfactory explanation of previous phenomenological expressions found to describe the behavior of $T_0(P)$ [29].

IV. CONCLUSIONS

A new equation describing the temperature and pressure dependence of the structural relaxation time $\tau(T,P)$ was derived from the Adam-Gibbs theory by introducing a suitable expression for the configurational entropy $S_c(T,P)$ consisting of a term related to the molar thermal expansion in addition to that obtained from the excess thermal heat capacity by Richert and Angell [4].

At a fixed pressure, for low pressures ($P \sim B$), this new equation reduces to a VFT equation with a fragility parameter independent from pressure, in agreement with the results

of several experiments undertaken in either isobaric and isothermal conditions.

The expression of $\tau(T, P)$ was successfully tested directly on the dielectric relaxation time data of an isobaric and two isothermal measurements on DGEBA. The involved parameters were estimated by the best fit of the data and their values agreed with those determined from the physical properties of the material. Considering that two of the four parameters (B and γ) were fixed at values calculated from data reported in the literature, the results of the best fit confirm the validity of the proposed expression [Eq. (9)] for describing the temperature and pressure behavior of the structural relaxation time.

Moreover, this approach provides an interpretation of the nonlinear dependence of T_0 and predicts a dependence of $T_0(P)$ [Eq. (10)] that agrees well with some expressions,

already discussed in literature, in which a quadratic dependence of T_0 on pressure was introduced on a phenomenological basis only.

Therefore the elegant description, based on the assumption of cooperatively rearranging regions, given in the Adam-Gibbs theory [5] also seems suitable to describe the pressure dependence of τ . Notwithstanding this encouraging result, at present we consider that further analysis on more systems are necessary to assess the actual limits of the proposed expression for τ .

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