Pressure and temperature dependence of structural relaxation dynamics in polymers: a thermodynamic interpretation

Daniele Prevosto, Simone Capaccioli, Mauro Lucchesi, Dino Leporini and Pierangelo Rolla

Department of Physics, University of Pisa, via F. Buonarroti 2, 56127, Pisa, Italy

E-mail: prevosto@df.unipi.it

Abstract

We analyse the slowing down of the structural relaxation dynamics of polymers in terms of the Adam and Gibbs theory. We consider a previously derived general relation between the configurational and the excess entropy, which was used to derive an analytical equation for the dependence of the structural relaxation time from the pressure and temperature. The model proved to successfully fit the relaxation dynamics of poly(methyl methacrylate), poly(propylene glycol) and poly(propylene glycol dimethylether), of different molecular weights, over a wide region of temperature and pressure values above the glass transition.

In the last few years, an intensive experimental effort has been made to study the glass transition as induced by pressure and temperature variations [1–7]. By using the possibility of inducing the glass transition through different thermodynamic paths, many studies principally focused on the investigation of the role of thermal energy and density reduction in slowing down structural dynamics [8–15]. These studies evidenced that the relative importance of these two quantities is strongly dependent on the properties of the systems investigated (type of interaction, molecular structure). However, in general it can be concluded that reductions of both thermal energy and density contribute to the slowing down of the structural dynamics on approaching the glass transition. Consequently, a general and satisfactory theory describing the increase of the relaxation time on approaching the glass transition must take into account both. Moreover, in the last few years some works showed that, in the dynamic region $\tau < 10^{-8}$ s, glassy systems whose isochronal dielectric spectra $\varepsilon(\nu)$ for different temperatures and pressures superpose [16] also follow a scaling relation between the isobaric relaxation time curves [16, 17], $\tau(T)$. Then, if the intermolecular interactions do not vary appreciably

with the thermodynamic state, a single thermodynamic parameter, which accounts for the role of the density and the thermal energy, rules the slowing down of the relaxation dynamics. In this respect, theories based just on the free-volume concept seem to be inadequate, as found by some experimental investigations [18, 19]. In contrast, the Adam and Gibbs (AG) theory [20] takes into account both the thermal energy and the density contribution. In fact, it relates the increase of the structural relaxation time, τ, on approaching the glass transition to the decrease of the configurational entropy, S_c:

$$\tau = \tau_0 \exp\left(\frac{C_{AG}}{T S_c}\right) \tag{1}$$

where T is the temperature, C_{AG} is a factor usually assumed to be independent on the temperature and on the pressure [20, 21], and τ_0 is the relaxation time value in the limit of infinitely high temperature. Unfortunately, the configurational entropy cannot be experimentally determined and consequently it is hard to perform a stringent test of equation (1), except by numerical and simulation work [21–24]. However, several works recently evidenced that near the glass transition the increase of the structural relaxation time is related to the decrease of the excess entropy of the melt with respect to the crystal (or to the glass), S_{exc}, according to the relation $\tau \propto \exp(B/(T S_{exc}))$ [25–28]. Moreover, the increase of the structural relaxation time during polymerization, and its temperature dependence in the non-equilibrium glassy state, can be rationalized in terms of the reduction of the excess entropy [29, 30]. These findings have usually been proposed as a verification of the AG theory. However, the debate about the relation between S_c and S_{exc} as well as some approximations used to test equation (1) remains open [31–38], and consequently the validity of the AG theory is still at the centre of a heated debate [32–35, 37].

In a recent work we proposed a simple and quite general relation between the excess and the configurational entropy. Using this relation we verified the AG theory both for temperature and pressure variations in two simple glass formers, and one polymer [39]. In this work we would like to verify the previous results for more systems, namely poly(propylene glycol) and poly(propylene glycol dimethylether), of different molecular weights (MW). Moreover, unlike in [39], we reconsider poly(methyl methacrylate) using a fully consistent set of thermodynamic and dynamic measurements performed on the same sample, and in the pressure interval 0.1–200 MPa we verify the negligible pressure dependence of the parameter C_{AG} (equation (1)).

1. Experimental details

In this work we analysed the relaxation dynamics of poly(methyl methacrylate) (PMMA) with MW 150 kg mol^{-1}, poly(propylene glycol) (PPG), and poly(propylene glycol dimethylether) (PPGM), with different molecular weights: PPG2000 (MW = 2000 g mol^{-1}), PPG3000 (MW = 3000 g mol^{-1}), PPGM1000 (MW = 1000 g mol^{-1}), and PPGM2000 (MW = 2000 g mol^{-1}). For the PPG and PPGM compounds we considered dielectric relaxation measurements by Suzuki [40], calorimetric measurements at atmospheric pressure of glassy and supercooled liquid by Park [41], and expansivity measurements of glassy and supercooled liquids from [42]. For the PMMA dielectric relaxation time, calorimetric and expansivity data are taken from Theobald [4].

2. Adam–Gibbs theory extended to pressure variation

The possibility of analysing relaxation data for different values of pressure and temperature gave the possibility of a stringent test of the AG theory, and made it necessary to extend the

relation $S_c(T) = C S_{exc}(T)$ [25, 26, 32] between the configurational and the excess entropies to the pressure contribution [17, 27, 28, 43]. With this purpose, recently we proposed [39] a quite general relation between the configurational and the excess entropy, that in the differential form is written as

$$dS_c(T, P) = \frac{\partial S_c(T, P)}{\partial T} dT + \frac{\partial S_c(T, P)}{\partial P} dP$$
$$= g_T(P)\frac{\partial S_{exc}(T, P)}{\partial T} dT + f_P(T)\frac{\partial S_{exc}(T, P)}{\partial P} dP \qquad (2)$$

where $g_T(P)$ and $f_P(T)$ are adimensional positive functions of pressure and temperature respectively, which need to be less than one ($dS_c < dS_{exc}$). The two functions $g_T(P) = (\partial S_c/\partial T)/(\partial S_{exc}/\partial T)|_{P=\text{const}}$ and $f_P(T) = (\partial S_c/\partial P)/(\partial S_{exc}/\partial P)|_{T=\text{const}}$ are expected to be different because $(\partial S_{exc}/\partial T)|_{P=\text{const}}$ includes configurational, harmonic, and anharmonic terms of the potential energy, whereas $(\partial S_{exc}/\partial P)|_{T=\text{const}}$, depending on the expansivity, has no contribution from the harmonic term of the potential energy [39]. Moreover, since the configurational entropy is a function of the state the condition

$$\frac{\partial}{\partial P}\left(g_T(P)\frac{\partial S_{exc}(T, P)}{\partial T}\right) = \frac{\partial}{\partial T}\left(f_P(T)\frac{\partial S_{exc}(T, P)}{\partial P}\right) \qquad (3)$$

must be satisfied. When equation (3) is satisfied, the variation of the configurational entropy can be calculated by integrating equation (2) along whichever thermodynamic path. In particular, when $S_c(T, P)$ is calculated along an isobaric path at atmospheric pressure, P_{atm}, from the initial temperature T_K to the final temperature T, and then an isothermal path at T up to the final pressure P, the configurational entropy is expressed by [39]

$$S_c(T, P) = g_T(P_{atm}) \int_{T_K}^{T} \frac{\Delta C_p}{T'} dT' - f_P(T) \int_{P_{atm}}^{P} \Delta\left(\frac{\partial V}{\partial T}\right)_{P'} dP' \qquad (4)$$

where T_K is defined as the temperature where $S_c(T_K, P = 0.1\ \text{MPa}) = 0$ (($\Delta C_p/T) dT = [(C_p^{melt} - C_p^{cryst})/T] dT$ and $\Delta(\partial V/\partial T)_p dP = -[(\partial V/\partial T)_P^{melt} - (\partial V/\partial T)_P^{cryst}] dP$ are the excess heat capacity and the excess expansion coefficient of the melt with respect to the crystal).

In equation (4) the excess entropy of the melt with respect to the crystal is considered. However, in polymers sometimes the thermodynamic properties of the crystalline state are not available, and the excess entropy with respect to the crystal cannot be calculated. In this case, since the temperature dependences of the volume and heat capacity of the crystal and the glass are similar, the properties of the crystal are evaluated as those of the glass [36].

Supposing that in equation (1) only the term $T S_c$ depends on T and P, we can explicitly predict the temperature and pressure dependence of the structural relaxation time by calculating the configurational entropy as a function of P and T using equation (4). We perform such calculations on the basis of three hypotheses: (1) the temperature dependence of the excess heat capacity is hyperbolic: $\Delta C_P = K/T$ [25, 41]; (2) the expansion coefficient of the crystal (glass) is pressure independent; (3) the pressure and temperature dependence of the volume of the melt is described by the Tait equation [44–46]

$$V(T, P) = V(T, 0)\left[1 - 0.0894 \ln\left(1 + \frac{P}{B(T)}\right)\right] \qquad (5)$$

where $V(T, 0)$ is the temperature dependence of the specific volume at zero pressure and $B(T) = b_1 \exp(-b_2 \times T)$ is a temperature dependent parameter related to the isothermal bulk coefficient [44, 46]. For practical calculations, $V(T, 0)$ can be approximated by $V(T, P = 0.1\ \text{MPa})$ [44]. According to these hypotheses we derive two equations representing

the extension to the pressure contribution of the AG theory:

$$\tau_\alpha(T, P) = \tau_0^\alpha \exp\left(\frac{DT_0^*}{T - T_0^*}\right) \tag{6}$$

$$T_0^*(T, P) = \frac{T_0}{1 + \frac{f_P(T)\delta B(T)}{g_T(P_{\mathrm{atm}})S_\infty}\left[-(\beta + \gamma - 1)\frac{p}{B(T)} + \gamma\left(1 + \frac{p}{B(T)}\right)\ln\left(1 + \frac{p}{B(T)}\right) - \ln\left(1 + \frac{p}{B(T)}\right)\right]} \tag{7}$$

where p is the value of the pressure relative to the atmospheric one ($P - 0.1$ MPa), T_0 is the diverging temperature at atmospheric pressure, the ratio f_P/g_T takes into account the 'proportionality' between S_c and S_{exc}, $D = C_{\mathrm{AG}}g_T$, $\delta = cb_2 V^{\mathrm{melt}}(T, p = 0)$, $\beta = 1/\delta((\partial V/\partial T)^{\mathrm{melt}} - (\partial V/\partial T)^{\mathrm{cryst}})_{p=0}$, $\gamma = (V_{\mathrm{melt}}b_2\backslash(\partial V/\partial T)_{p=0}^{\mathrm{melt}})^{-1}$, and S_∞ is the excess entropy at atmospheric pressure in the limit of infinite temperature [25]. In our derivation, S_∞ is used only as a parameter related to the heat capacity integral appearing in equation (4) ($S_\infty = K/T_0$) so our analysis is not in any way affected by the physical meaning of considering the excess entropy of the liquid at infinite temperature.

For $p = 0$, T_0^* reduces to T_0 and equation (6) reduces to the Vogel–Fulcher–Tammann (VFT) function for the temperature dependence of the structural relaxation time [47]. Moreover, for low values of pressure ($P < B(T)$), the leading order terms of equations (6) and (7) reduce to a VFT-like equation for the pressure dependence of the structural relaxation time, as often used to fit data [48, 49]. However, for $B \geqslant P$ higher order terms become important and equations (6) and (7) substantially deviate from the VFT-like equation.

It is important to note that on the basis of simulation a negligible variation of C_{AG} with pressure was demonstrated for density changes of the order of 20% [21, 22] (typical density variations in experiments are of the order of 5–10%). Moreover, the negligible pressure dependence of $(\partial V/\partial T)^{\mathrm{cryst}}$ is found for several systems up to pressures of the order of hundreds of megapascals [4, 12, 44]. On the basis of these findings we retain the well justified assumptions that we made in deriving equation (7).

3. Results and discussion

3.1. Thermodynamic data

PMMA expansivity measurements on the melt (0.1 MPa $< P <$ 300 MPa and 380 K $< T <$ 460 K) and on the glass (0.1 MPa $< P <$ 400 MPa and 300 K $< T <$ 430 K, from [4]) were fitted according to the Tait equation (figure 1). The Tait equation reproduces the data for both the melt and the glassy states with the parameters reported in table 1. Expansivity data on the melt state for PPG2000, PPG3000, PPGM1000, and PPGM2000 are published as a function of pressure and temperature in [42]. The Tait equation reproduces these data well in the ranges 0.1–180 MPa and 303–473 K (figure 1) with the parameters as in table 1.

Heat capacity data for the PMMA and PPG compounds were taken from [4, 41]. From the data on the melt and the glass we estimated the excess heat capacity of the melt with respect to the glass in the region of supercooled liquid. Then we fitted the temperature dependence of the excess heat capacity according to the hyperbolic function $\Delta C_p = C/T$. From these data we calculated the isobaric excess entropy of these systems, which is $S_{\mathrm{exc}}^{\mathrm{isob}}(T) = S_\infty - C/T$. The values of S_∞ for these systems are 0.59 ± 0.02 J mol^{-1} K^{-1} for PPG2000, 0.58 ± 0.02 J mol^{-1} K^{-1} for PPG3000, and 0.35 ± 0.02 J mol^{-1} K^{-1} for PMMA. These values, calculated from the excess of the heat capacity of the liquid with respect to the crystal, are estimates of the excess entropy of the liquid with respect to the crystal within a few per cent.
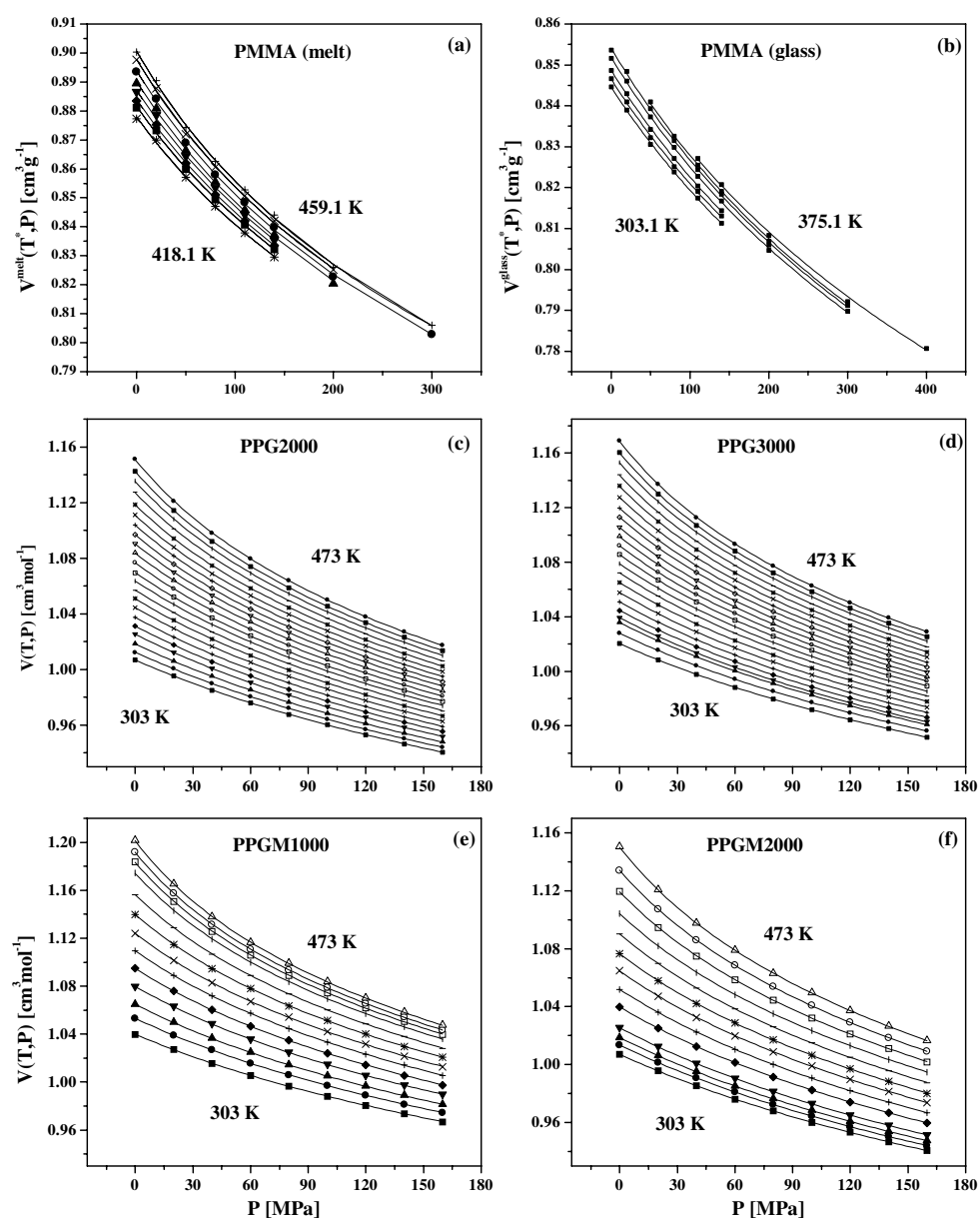
Figure 1. Volumetric measurements under different isothermal conditions as a function of pressure for: (a) PMMA melt; (b) PMMA glass; (c) PPG2000; (d) PPGM2000; (e) PPGM1000; (f) PPG3000 [4, 42]. Curves are fitting curves, for the Tait equation.

3.2. Relaxation time data

The analysis of the PMMA data on the basis of the AG theory has already been published by us [39]. However, the previous analysis was performed using thermodynamic and dynamic data on samples with different molecular weights. In this work we analysed thermodynamic and dynamic data on the same sample with MW 150 kg mol^{-1}. In [4] relaxation time data are reported under isobaric conditions in the range 0.1–400 MPa and in the temperature interval

Table 1. Parameters of the Tait equation.

	$V(T, p = 0)$ (cm^3 g^{-1})	$B(T)$ (MPa)
PMMA (melt)	$0.728 + 2.01 \times 10^{-4} \times T + 3.7 \times 10^{-7} \times T^2$	$1520 \exp(-5.3 \times 10^{-3} \times T)$
PMMA (glass)	$0.793 + 1.72 \times 10^{-4} \times T$	$414 \exp(-1.6 \times 10^{-3} \times T)$
PPG2000 (melt)	$0.863 + 2.34 \times 10^{-4} \times T + 7.9 \times 10^{-7} \times T^2$	$717 \exp(-5.2 \times 10^{-3} \times T)$
PPG3000 (melt)	$0.853 + 2.92 \times 10^{-4} \times T + 7.17 \times 10^{-7} \times T^2$	$703 \exp(5.19 \times 10^{-3} \times T)$
PPGM1000 (melt)	$0.912 + 8.37 \times 10^{-5} \times T + 1.13 \times 10^{-6} \times T^2$	$772 \exp(5.75 \times 10^{-3} \times T)$
PPGM2000 (melt)	$0.875 + 2.3 \times 10^{-4} \times T + 8.23 \times 10^{-7} \times T^2$	$716 \exp(-5.3 \times 10^{-3} \times T)$

Table 2. Parameters of the VFT equation for fitting atmospheric pressure data.

	τ_0 (ps)	D	T_0 (K)
PMMA	10 ± 4	4 ± 1	337 ± 14
PPG2000	1.25 ± 0.25	4.69 ± 0.13	174.8 ± 0.8
PPG3000	0.46 ± 0.04	5.40 ± 0.23	171.8 ± 0.8
PPGM1000	0.19 ± 0.04	6.18 ± 0.10	159.1 ± 0.3
PPGM2000	0.54 ± 0.09	5.31 ± 0.18	164.4 ± 1

370–465 K. The analysis of the data is carried out only up to 200 MPa, since for higher pressure values the quality of data is much poorer.

Dielectric measurements at atmospheric pressure as a function of temperature and under three isothermal conditions as a function of pressure were performed by Suzuki on PPG and PPGM samples for frequencies up to 1.5 MHz [40]. By the analysis he found that the shape of the structural process is almost constant over the whole interval considered [40], and by using this property he collapsed the spectra onto a master curve, obtaining structural relaxation time data up to the ns range. In order to avoid the data being derived by extrapolating over a large temperature interval, we analysed only relaxation times of the loss peak greater than 10^{-8} s. Moreover, we do not consider the relaxation times measured under isothermal conditions at 320 and 319 K for PPGM1000 and PPGM2000, which are obtained by a large extrapolation procedure [40].

As the parameter representing the relaxation time we used the characteristic time corresponding to the frequency of the dielectric loss peak: $\tau_{\max} = 1/(2\pi \nu_{\max})$, which is a model independent parameter. Moreover, since the structural process for the systems investigated is shape invariant for the temperature and pressure intervals considered [40], the temperature dependence of $\tau_{\max}$ is proportional to that of any other parameter representing the characteristic relaxation time. The analysis of the data was performed as follows:

(I) we fitted the relaxation time data at atmospheric pressure using VFT, obtaining the values of τ_0, D, and T_0 [12, 25, 40];

(II) we fitted the relaxation time data at higher pressures with equations (6) and (7) using the values of D, T_0, and τ_0 obtained from the fit at atmospheric pressure, and the values of the thermodynamic parameters (δ, β, γ, $B(T)$) calculated from thermodynamic data.

Consequently, in the case of PMMA, where expansivity and calorimetric measurements for the melt and for the glass are available, the only free parameter in fitting the relaxation time data at $P > 0.1$ MPa is the ratio $g_T(P_{\text{atm}})/f_P(T)$. For PPG and PPGM, where the expansivity data for the glass and the calorimetric measurements are not available, relaxation time data for $P > 0.1$ MPa are fitted with only two free parameters: $S'_\infty = g_T(P_{\text{atm}})/f_P(T)S_\infty$ and β.
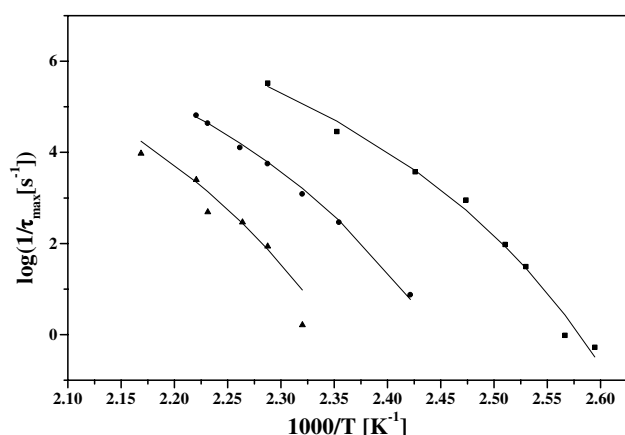
Figure 2. Relaxation time data in isobaric conditions at 0.1 (squares), 100 (circles), and 200 (upward-pointing triangles) MPa for PMMA [4]. The curves are fitting curves, with equations (6) and (7).
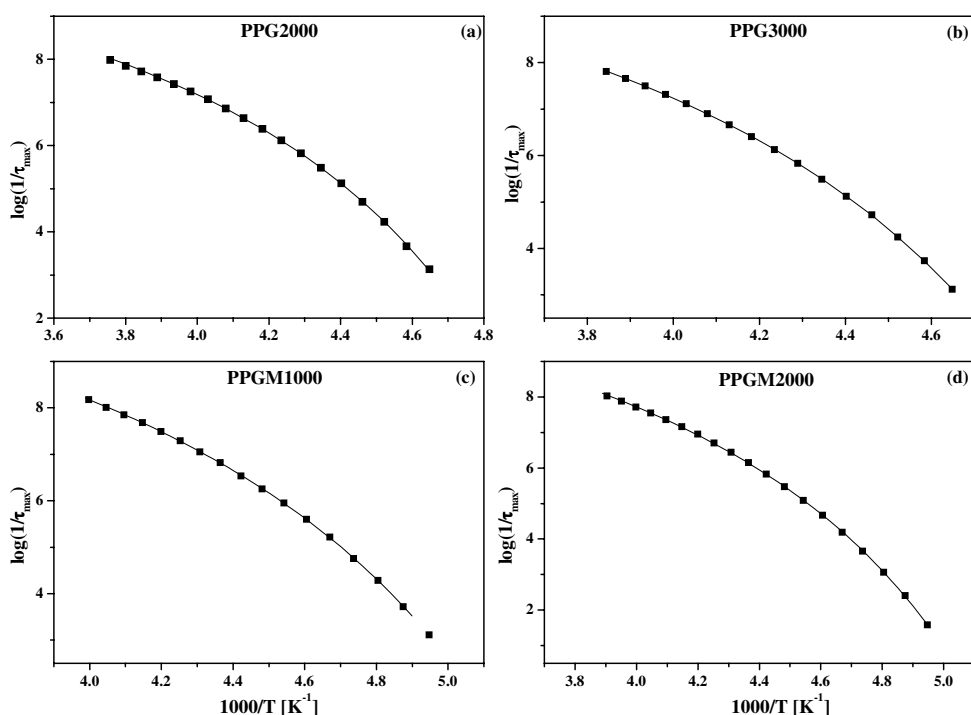

Figure 3. Relaxation time data at atmospheric pressure for (a) PPG2000, (b) PPG3000, (c) PPGM1000, (d) PPGM2000 as a function of temperature [40]. The curves are fitting curves, with the VFT equation.

The parameters of the fit of the atmospheric pressure data for all polymers are listed in table 2 (figures 2 and 3).

For PMMA equations (6) and (7) fitted the temperature dependence of the structural relaxation time at both 100 and 200 MPa (figure 2), with $g_T(P_{atm})/f_P(T) = 1.4 \pm 0.1$.

For PPG and PPGM equations (6) and (7) reproduce the pressure dependence of the structural relaxation time well under several isotherm conditions (figure 4). The values of the parameters obtained from the analysis are reported in table 3. By using the values of S_∞ and S'_∞ (S_∞ is calculated from the calorimetric data on the glass and the melt) we can estimate
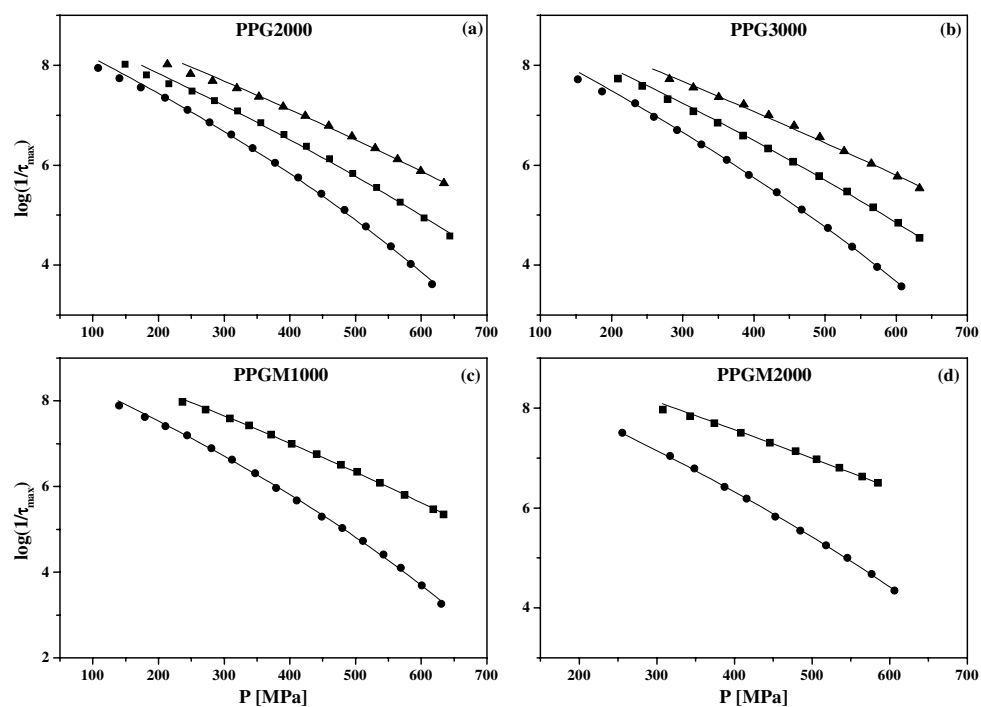
Figure 4. Experimental data on structural relaxation times (symbols) for: (a) PPG2000 and (b) PPG3000 at 293 (circles), 303 (squares), and 313 (upward-pointing triangles) K; (c) PPGM2000 at 286 (circles), and 303 (squares), K; (c) PPGM1000 at 283 (circles), and 303 (squares) [40]. The curves are fits with equations (6) and (7).

Table 3. Parameters from the fit of relaxation time data at $P > 0.1$ MPa. In the last column the value of S_∞ from calorimetric measurements is reported when available.

	β			S'_∞ (J mol^{-1} K^{-1})			S_∞ (J mol^{-1} K^{-1})
T (K)	293	303	312	293	303	312	
PPG2000	1.29 ± 0.01	1.30 ± 0.01	1.30 ± 0.01	0.63 ± 0.05	0.62 ± 0.04	0.61 ± 0.04	0.59 ± 0.02
PPG3000	1.28 ± 0.01	1.29 ± 0.01	1.30 ± 0.01	0.60 ± 0.03	0.60 ± 0.03	0.60 ± 0.03	0.58 ± 0.02
T (K)	283	303		283	303		
PPGM1000	1.27 ± 0.01	1.28 ± 0.01		0.68 ± 0.03	0.64 ± 0.03		
PPGM2000	1.33 ± 0.01 (286 K)	1.33 ± 0.01		0.69 ± 0.03 (286 K)	0.67 ± 0.03		

$g_T(P_{\mathrm{atm}})/f_P(T)$: 1.05 ± 0.08 and 1.04 ± 0.08 for PPG2000 and PPG3000, respectively. This result reflects the fact that in these systems the relative weights with which the isothermal and the isobaric configurational entropies contribute to the excess one are nearly the same. For PPGM, since the value of S_∞ cannot be estimated, the ratio g_T/f_P cannot be calculated. As a test of the coherence of the fit we observe that S'_∞ for PPG and PPGM are very similar, as expected since the two systems have similar molecular structures.

As regards the value of g_T/f_P, two remarks are important. First, the values are different for PMMA and PPG, reflecting these two systems having very different relaxation behaviours:
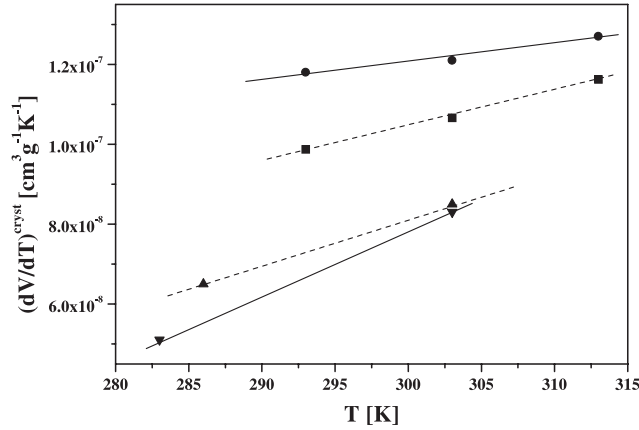
Figure 5. The expansion coefficient obtained from the fit of the relaxation time data for PPG2000 (squares), PPG3000 (circles), PPGM1000 (upward-pointing triangles), and PPGM2000 (downward-pointing triangles). Lines are guides for the eyes.

in particular, PMMA shows a strong secondary relaxation process, which on the frequency scale is very close to the structural one. This secondary process probably contributes to the configurational entropy [50], thus varying the percentage of the configurational contribution to the excess entropy with respect to systems with small secondary processes, such as PPG. As a second issue, we note that since the configurational entropy defined in equation (2) must be a function of the state, the parameters g_T and f_P must be related to each other. This relation can be derived by solving equation (3) which, by using the fundamental relation of thermodynamics, can be rewritten as

$$\Delta \left(\frac{\partial^2 V}{\partial T^2} \right) \left(f_p(T) - g_T(P) \right) = \frac{\partial g_T(P)}{\partial P} \frac{\Delta C_P}{T} - \frac{\partial f_P(T)}{\partial T} \Delta \left(\frac{\partial V}{\partial T} \right). \qquad (8)$$

According to equation (8), when g_T and f_P are constant and not equal, the configurational entropy in equation (4) is a function of the state only if $\Delta(\partial^2 V/\partial T^2) = 0$. It is noteworthy that, in the temperature region where we verify the AG theory, $T_g < T < 1.2T_g$, $\Delta V(T)$ can be described as a linear function of temperature, and $\Delta(\partial^2 V/\partial T^2) = 0$ is approximately true. For this condition $g_T(P)$ and $f_p(T)$ can be approximated by two constants with different values, without violating any thermodynamic principle. Nevertheless, using the expansivity data for our systems we verified that the expected variation of $f_p(T)$, due to the departure of $\Delta(\partial^2 V/\partial T^2)$ from zero, is also smaller than the experimental error in the particular case when $(\partial g_T/\partial P) = 0$. In fact, equation (8) can be rewritten as

$$\Delta \left(\frac{\partial^2 V}{\partial T^2} \right) \Big/ \Delta \left(\frac{\partial V}{\partial T} \right) = \frac{1}{\left(-f_p(T) + g_T(P) \right)} \frac{\partial f_P(T)}{\partial T} > \frac{\partial f_P(T)}{\partial T} \qquad (9)$$

where the last part is justified because $g_T - f_P$ is less than unity. From equation (9) we derive that the temperature variation of f_p is of the order of $\Delta(\frac{\partial^2 V}{\partial T^2})/\Delta(\frac{\partial V}{\partial T})$ (about 10^{-3} for normal systems); moreover, since f_P is of the order of unity this is also its relative temperature variation. According to this evaluation we can easily derive that the relative variation of f_P is 10^{-3} and in the temperature interval that we consider (about 50 K) f_P is expected to vary by about 5%. Since from the fit we obtain f_P with an error of about 8%, this variation cannot be detected in our analysis.

The parameter β yields the expansion coefficient of the crystal, $(\partial V/\partial T)_P^{\mathrm{cryst}}$, at the temperature of the dielectric isothermal measurements: the values are reported in figure 5. The expansion coefficients have the right order of magnitude, as deduced from the comparison with the data for the melt; moreover, as expected, they increase with the temperature.
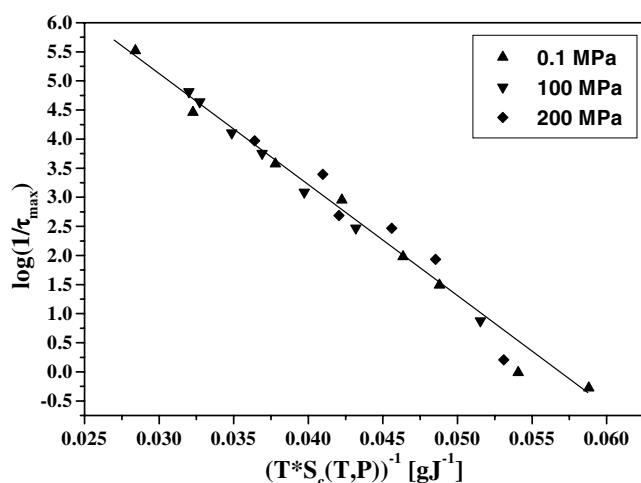
Figure 6. Relaxation time data for PMMA (symbols) as a function of $(T^*(S_{exc}^{isob} + f_P/g_T S_{exc}^{isot}))$ in the temperature interval 370–465 K and pressure interval 0.1–200 MPa. The line is a linear regression of the data.

The pressure dependence of the structural relaxation time has usually been fitted with a VFT equation, which reproduces the experimental data well [48, 49]. Also for PPG the pressure dependence of the structural relaxation time has been fitted with a VFT equation by several authors [2, 40]. Anyway, the unphysical values of the parameters obtained from the analysis were recognized, as well as the fact that three parameters of the VFT assume different values when the different isothermal measurements are considered [40, 48, 49]. According to equations (6) and (7) the pressure dependence of the structural relaxation time up to 600 MPa is no longer described by a VFT function. However, in spite of the complexity of equations (6) and (7), our analysis is performed with many fixed parameters, and only a few that change in accordance with the typical behaviour of the expansivity data. The close connection of the parameters in equations (6) and (7) with the thermodynamic properties of the system allows a check on the reliability of the fit, and in our opinion supports the use of our equation against the use of the VFT equation. Moreover, in order to verify the deviation of the pressure dependence of the structural relaxation time from the VFT function it is possible to investigate the deviation of the Stickel variable, $\Phi_{1/\tau} = \{[d\log(1/\tau_{max})]/d(P)\}^{-1/2}$ [48–54], from the linear pressure dependence. We performed this analysis on PPG and PGM data but no reliable conclusion can be drawn because of the scatter of the data.

An equivalent, but more direct, test of the AG model can be performed on PMMA data. With the functional forms estimated for the temperature dependence of the heat capacity and the temperature and pressure dependence of the expansivity of the melt and the glassy state, we calculated S_{exc}^{isob} and S_{exc}^{isot} in the same temperature and pressure intervals as the relaxation time data. Then, considering that $S_c = g_T(S_{exc}^{isob} + f_P/g_T S_{exc}^{isot})$ (equation (4)), we plotted $\log(1/\tau_{max})$ data as a function of $T^*(S_{exc}^{isob} + f_P/g_T S_{exc}^{isot})$ and verified the possibility of obtaining a linear representation of data with appropriate values of f_P/g_T. We found that in accordance with the previous analysis a single value of the coefficient $g_T/f_P = 1.4 \pm 0.1$ is sufficient for reducing all the data obtained for different pressure values onto a single master curve within experimental error (figure 6). The fitting of all the data with a first-order polynomial provides the intercepts with the y-axis, $\log(1/\tau_0) = 11.1 \pm 0.3$, and the slope of the straight line, $C_{AG}/g_T = -197 \pm 6$ J kmol^{-1}, with a correlation coefficient $r = 0.99$ and a standard deviation SD $= 0.24$. This analysis confirms that the three data sets can be described by the same curve. Moreover, since the slope (C_{AG}/g_T) is constant with varying pressure, we can conclude from a direct analysis that the pressure dependence of C_{AG}/g_T in PMMA is negligible up to 200 MPa.

It is important that according to our analysis the parameter $(T S_c)$ alone is sufficient for describing the increase of the structural relaxation time on approaching the glass transition in several systems. Moreover, as reported from previous analysis [40], at least for PPG and PPGM it was observed that the shape of the structural peak is independent of pressure and temperature in the region near the glass transition (for PMMA we have not found any reference). This result was also found for o-terphenyl and triphenylchloromethane which were previously considered by us for verifying equations (6) and (7). Then, in these systems, the product $(T S_c)$ is the only parameter necessary for reproducing the evolution of the structural process on approaching the glass transition.

4. Conclusions

We analysed the combined pressure–temperature dependence of structural relaxation time polymers by a suitable extension of the AG theory. It is worth noting that even if the experimental data on dynamic and thermodynamic properties of these systems have been yet published, their analysis on the basis of the AG model is the original contribution of this work. The equations used for the analysis of relaxation time data are derived with few and reasonable assumptions:

- the parameter C_{AG} in equation (1) is temperature and pressure independent in the region near the glass transition;
- the excess and the configurational entropy are related through equation (2);
- the temperature dependence of the excess heat capacity is described by the hyperbolic equation;
- the pressure dependence of the expansion coefficient of the crystal (glass) is negligible.

It is worth noting that the first and the third assumptions were directly verified: for PMMA the parameter C_{AG} is constant for pressure up to 200 MPa, and the temperature dependence of the excess heat capacity was fitted to the hyperbolic approximation for PMMA and PPG systems.

Equations (6) and (7) describe satisfactorily the variation of the structural relaxation times on approaching the glass transition. All the parameters in the equations are related to calorimetric and expansivity properties of the system. The analysis of the data at high pressure is performed with one free parameter for PMMA and two free parameters for PPG and PPGM. The best-fit parameters have reasonable values, and this finding confirms the validity of our analysis.

In conclusion, comparing also with previous results on many systems [17, 27, 28, 39] we think that in those systems where the shape of the structural process remains almost constant on approaching the glass transition, the evolution of the structural process can be reproduced by the use of one thermodynamic quantity. In particular, the product $T S_c$ appears to be suitable for describing this evolution since equations (6) and (7) give a good description of the variation of structural relaxation times on approaching the glass transition.

References

[1] McCrum N G, Read B E and Williams G 1967 *Anelastic and Dielectric Effects in Polymeric Solids* (New York: Dover)
[2] Andersson S P and Andersson O 1998 *Macromolecules* **31** 2999

[3] Paluch M 2000 *J. Phys.: Condens. Matter* **12** 9511

[4] Theobald S, Pechhold W and Stoll B 2001 *Polymer* **42** 289

[5] Solunov Chr 2002 *J. Phys.: Condens. Matter* **14** 7297

[6] Roland C M, Psurek T, Pawlus S and Paluch M 2003 *J. Polym. Sci.* B **41** 3047

[7] Paluch M, Patkowski A and Fischer E W 2000 *Phys. Rev. Lett.* **85** 2140

[8] Ferrer M L, Lavrence C, Demirjian B G, Kivelson D, Alba-Simonesco C and Tarjus G 1998 *J. Chem. Phys.* **109** 8010

[9] Casalini R and Roland C M 2003 *J. Chem. Phys.* **119** 11951

[10] Roland C M and Casalini R 2003 *Macromolecules* **36** 1361

[11] Mpoukouvalas K and Floudas G 2003 *Phys. Rev.* E **68** 031801

[12] Naoki M, Endou H and Matsumoto K 1987 *J. Phys. Chem.* **91** 4169

[13] Paluch M, Casalini R and Roland C M 2002 *Phys. Rev.* B **66** 092202

[14] Paluch M, Casalini R, Patkowski A, Pakula T and Roland C M 2003 *Phys. Rev.* E **68** 031802

[15] Paluch M, Casalini R, Roland C M, Meier G and Patkowski A 2003 *J. Chem. Phys.* **118** 4578

[16] Corezzi S, Rolla P A, Paluch M, Ziolo J and Fioretto D 1999 *Phys. Rev.* E **60** 4444

[17] Capaccioli S, Lucchesi M, Casalini R, Presto S, Rolla P A, Viciosa M T, Corezzi S and Fioretto D 2002 *Phil. Mag.* B **82** 651

[18] Paluch M, Casalini R and Roland C M 2003 *Phys. Rev.* E **67** 021508

[19] Corezzi S, Capaccioli S, Casalini R, Fioretto D, Paluch M and Rolla P A 2000 *Chem. Phys. Lett.* **320** 113

[20] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **28** 139

[21] Scala A, Starr F W, La Nave E, Sciortino F and Stanley H E 2000 *Nature* **406** 166

[22] Sastry S 2001 *Nature* **409** 164

[23] Starr F W, Angell C A and Stanley H E 2003 *Physica* A **323** 51

[24] Speedy R J 2001 *J. Chem. Phys.* **114** 9069

[25] Richert R and Angell C A 1998 *J. Chem. Phys.* **108** 9016

[26] Fitz B D and Mijovic J 2000 *Macromolecules* **33** 887

[27] Casalini R, Capaccioli S, Lucchesi M, Rolla P A and Corezzi S 2001 *Phys. Rev.* E **63** 031207

[28] Casalini R, Capaccioli S, Lucchesi M, Rolla P A, Paluch M, Corezzi S and Fioretto D 2001 *Phys. Rev.* E **64** 041504

[29] Corezzi S, Fioretto D and Rolla P A 2002 *Nature* **420** 654

[30] Hutchinson J M, Montserrat S, Calventus Y and Corte's P 2000 *Macromolecules* **33** 5252

[31] Phillips W A, Buchenau U, Nucker N, Dianoux A J and Petry W 1989 *Phys. Rev. Lett.* **63** 2381

[32] Angell C A and Borick S 2002 *J. Non-Cryst. Solids* **307–310** 393
    Johari G P 2002 *J. Non-Cryst. Solids* **307–310** 387

[33] Ngai K L 1999 *J. Phys. Chem.* B **103** 5895

[34] Johari G P 2000 *J. Chem. Phys.* **112** 7518

[35] Johari G P 2003 *J. Chem. Phys.* **119** 635

[36] Martinez L M and Angell C A 2002 *Nature* **410** 663

[37] Speedy R J 2001 *J. Phys. Chem.* B **105** 11737

[38] Yamamuro O, Tsukushi I, Lindqvist A, Takahara S, Ishikawa M and Matsuo T 1998 *J. Phys. Chem.* B **102** 1605

[39] Prevosto D, Lucchesi M, Capaccioli S, Casalini R and Rolla P A 2003 *Phys. Rev.* B **67** 17420

[40] Suzuki A, Masuko M and Wakisaka K 2002 *Tribol. Int.* **35** 55

[41] Park I, Saruta K and Kojima S 1998 *J. Phys. Soc. Japan* **67** 4131

[42] Zoller P and Walsh D J 1995 *Standard Pressure–Volume–Temperature Data for Polymers* (Lancaster, PA: Technomic)

[43] Casalini R, Paluch M, Fontanella J J and Roland C M 2002 *J. Chem. Phys.* **117** 4901

[44] Van Krevelen D W 1997 *Properties of Polymers* (Amsterdam: Elsevier)

[45] Schlosser H and Ferrante J 1989 *J. Phys.: Condens. Matter* **1** 2727

[46] Lorenzen M, Bösecke P, Ferrero C, Riekel C and Eichler A 1997 *Macromolecules* **30** 6645

[47] Casalini R, Paluch M, Psurek T and Roland C M 2004 *J. Mol. Liq.* **111** 53

[48] Paluch M, Rzoska S J, Habdas P and Ziolo J 1998 *J. Phys.: Condens. Matter* **10** 4131

[49] Paluch M and Ziolo P 1998 *Europhys. Lett.* **44** 317

[50] Gangasharan and Murthy S S N 1993 *J. Chem. Phys.* **99** 9865

[51] Stickel F, Kremer F and Fischer E W 1993 *Physica* A **201** 318

[52] Stickel F, Fischer E W and Richert R 1995 *J. Chem. Phys.* **102** 6251

[53] Stickel F, Fischer E W and Richert R 1996 *J. Chem. Phys.* **104** 2043

[54] Casalini R, Paluch M and Roland C M 2002 *J. Chem. Phys.* **118** 5701