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Effect of pressure on the dynamics of glass formers

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A description of the pressure dependence of the structural relaxation time has been derived from the Adam-Gibbs theory by writing the configurational entropy in terms of the excess heat capacity and the molar thermal expansion. This new equation was tested successfully on dielectric relaxation data for an epoxy compound over a wide range of temperature and pressure.

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One of the major challenges in condensed matter physics is to understand the ability of some materials to avoid crystallization during cooling below their melting temperature, even when only moderate cooling rates are applied. In the supercooled state the relaxation time τ and the viscosity η increase dramatically with decreasing temperature and the glassy state is conventionally defined as the state in which the material cannot reach equilibrium within a time period of 100 s. The glassy state can be induced either by decreasing the temperature or increasing the pressure of the system. However, for many materials the pressure required to approach the glass transition is very high, therefore the glass transition has been mostly studied by measuring the temperature dependence of viscosity and relaxation time. Nevertheless, a full study of the temperature and pressure dependence of the relaxation time and viscosity can give a very interesting insight for the understanding of the glass transition and allows a more stringent test of theoretical models [1].

The Adam-Gibbs (AG) model [2] provides an expression for the relaxation time that contains the configurational entropy, S_c

$$\tau=\tau_o \exp\left(\frac{C_{AG}\Delta\mu}{TS_c}\right), \tag{1}$$

where $\Delta\mu$ is the free energy barrier (per molecule per cooperative rearranging region) to rearrangements, T is the absolute temperature, τ_o is the relaxation time at very high temperatures, C_{AG} is a constant, and $S_c(T)$ is defined as the excess entropy, $S_c(T)=S^{melt}-S^{crystal}$, and measures all the entropy of the melt apart from the vibrational contribution. At atmospheric pressure the dependence of S_c on the temperature, as calculated from the excess heat capacity ΔC_p, of the melt respect to the crystal, is well described as $S_c(T)=S_\infty-k/T$, where k is a constant and S_∞ is the limit of S_c at very high temperatures [3,4]. By substituting this expression for $S_c(T)$ in Eq. (1) a Vogel-Fulcher-Tammann (VFT) dependence of the relaxation time is found

$$\tau=\tau_o \exp\left(\frac{DT_o}{T-T_o}\right), \tag{2}$$

where the fragility parameter is $D=C_{AG}\Delta\mu/k$ and the Vogel temperature is $T_o=T_K=k/S_\infty$ (with T_K the Kauzmann temperature) [3]. The agreement between the temperature dependence of the structural relaxation time and experimental data of $S_c(T)$ for several glass formers was recently shown by Richert and Angell [3]. Some limitations to the AG theory were recently pointed out, in particular, how this theory may fail to take into consideration some kinetic aspects of the glass transition [5,6]. Nevertheless, this theory seems to give an interesting insight for the understanding of the role of pressure in controlling the glass transition and, in particular, if its effect can be explained in the conceptual frame of thermodynamics.

Recently, a new equation to describe both pressure and temperature dependence of the relaxation time, $\tau(T,P)$, was derived starting from the original result of the AG theory [Eq. (1)] [7]. The pressure dependence of the configurational entropy was estimated by including a term related to the molar thermal expansion together with the contribution related to excess heat capacity [8]

$$S_c(T,P)=\int_{T_K}^{T}\frac{\Delta C_P(T')}{T'}dT'-\int_0^P \Delta\left(\frac{\partial V}{\partial T}\right)_{P'}dP', \tag{3}$$

where $\Delta C_P(T)=k/T$ and $\Delta(\partial V/\partial T)_P=(\partial V/\partial T)_P^{melt}-(\partial V/\partial T)_P^{cryst}$ is the difference of the molar thermal expansivity of the melt and the crystal, respectively. Therefore, the effect of the pressure is taken into account in the integral of the molar excess thermal expansivity and, by compressing the material, an isothermal reduction of the configurational entropy is expected. However, evidently the excess expansivity integral is expected to have a finite limit for $P\rightarrow\infty$ [9] and the condition $S_c(T,P)\geqslant 0$ has to be satisfied at any T and P.

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In general, the substitution of Eq. (3) in Eq. (1), yields a VFT-like expression for $\tau(T,P)$ in which the Vogel temperature is substituted by the temperature $T_o^*(T,P)$ defined as

$$T_o^*(T,P)=\frac{T_o}{1-\frac{1}{S_\infty}\int_0^P \Delta\left(\frac{\partial V}{\partial T}\right)_{P'} dP'}, \tag{4}$$

while the fragility parameter D results independent of pressure, with the condition that $\Delta\mu$ does not change. As a consequence, if the temperature dependence of the excess expansivity integral is negligible, T_o^* is dependent only on pressure, and $\tau(T,P)$ data at a fixed pressure should be described by VFT equations with the same fragility parameter D. This behavior agrees with the results of several high pressure experiments on different glass formers [10–15].

The evaluation of the integral in Eq. (4) requires values of the volume of both melt and crystal state. The pressure and temperature dependence of the thermal expansivity of the melt was estimated by using the Tait equation [16,17] $V(T,P)=V(T,0)[1-C\ln(1+P/B(T))]$ where C is a dimensionless constant and $B(T)$ is a temperature dependent factor with the same dimension as pressure that can be expressed by $B(T)=b_1\exp(-b_2T)$ [18]. Both the value and the pressure dependence of the crystal thermal expansivity are usually smaller than that of the melt; as no complete set of data were available, at first approximation $(\partial V/\partial T)_P^{cryst}$ was considered independent of pressure and fixed to the value at atmospheric pressure. This approximation was found to be correct for the calculation of Eq. (4) up to very high pressure [for $P/B(T)<2$] [19]. Consequently in the present paper, being $B\sim300$ MPa (considering the typical values for liquids $b_1\sim10^3$ MPa and $b_2\sim4\times10^{-3}$ K^{-1} [16]), this approximation is expected to have only a minor influence in the pressure range investigated.

As a result, by calculating the integral of the excess thermal expansivity the following expression for $T_o^*(T,P)$ was found [7]:

$$T_o^*(T,P)=\frac{T_o}{\left\{1+\frac{\delta}{S_\infty}\left[-(\beta+\gamma-1)P+[(\gamma-1)B(T)+\gamma P]\ln\left(1+\frac{P}{B(T)}\right)\right]\right\}}, \tag{5}$$

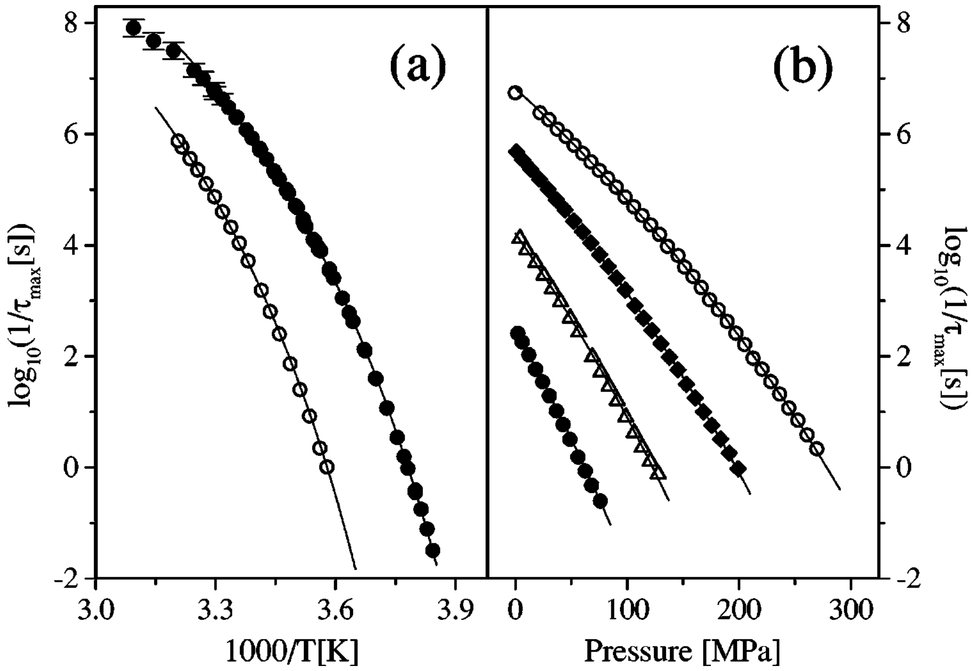

FIG. 1. Structural relaxation time data, $\log_{10}(1/\tau[s])$: (a) obtained from dielectric relaxation at ambient pressure (solid circles) and at $P=95.5$ MPa (open circles) vs. reciprocal of temperature; (b) obtained from dielectric relaxation at $T=303.4$ K (open circles), $T=293$ K (solid diamonds), $T=283$ K (open triangles), and $T=274.5$ K (solid circles) vs pressure. When not reported the error bars are smaller than the symbol size. The solid lines are the best fits obtained by using T_o substituted by T_o^* [Eq. (5)], the parameters are reported in Table I.

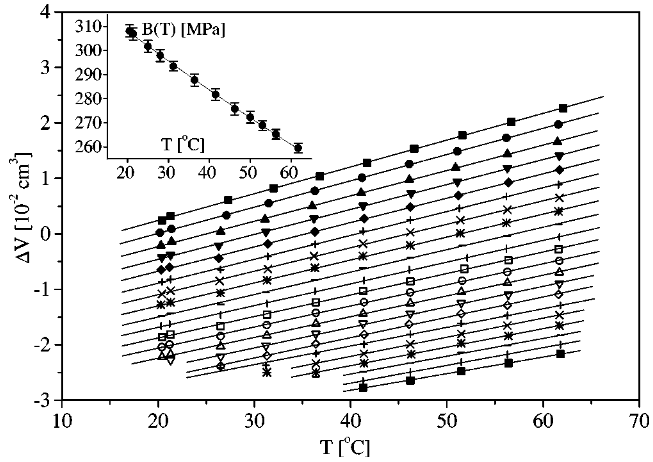

FIG. 2. Variation of the volume with temperature at different pressure. The data are referred to a quantity of 1.021 g of PPGE. The pressure was, from top to bottom, from 0.1 MPa to 200 MPa by step of 10 MPa. The solid lines are linear fit to the data. In the inset is shown the value of $B(T)$ estimated at the different temperatures and the best fit to the equation $B(T)=b_1\exp(-b_2T)$ (solid line).

where the parameters β, γ, and δ are related to the thermal expansion coefficient at atmospheric pressure, $\alpha=1/V(\partial V/\partial T)_{Patm}$ and the molar volume of the melt and the crystal, V^{melt} and V^{cryst}, respectively, being $\delta=CV^{melt}(T,0)b_2$, $\beta=[\Delta(\partial V/\partial T)_{Patm}]/\delta$, and $\gamma=\alpha/b_2$.

It has to be noted that the parameters β, γ, and δ in Eq. (5) can be considered almost independent of temperature, and the variation of $B(T)$, although appreciable, has only weak repercussions on T_o^*, provided that the investigated temperature range $\Delta T<1/b_2$ and $P\leqslant B(T)$ [19]. In these conditions, the temperature variation of T_o^* is smaller than the experimental sensitivity and, therefore, T_o^* can be considered dependent on the pressure only, though deviations from the VFT behavior for isobaric measurements should be expected at very high pressure.

In the analysis of the experimental data in terms of this modified AG model, the values of the parameters $B(T)$, β, γ, and δ can be directly derived from the thermal expansivity properties of the investigated material. In a first test this model was found to well describe the dielectric relaxation measurements for two different materials [7,20] and the values for the fit parameters were reasonably close to what calculated from the typical thermal expansivity data found in the literature for polymers and liquids.

In this paper we investigated the temperature and pressure behavior of poly(phenyl glycidyl ether)-co-formaldehyde (PPGE)($M_w=348$). The model was tested on six different sets of data for $\tau(T,P)$ (estimated as $\tau=1/2\pi\nu_{max}$) measured by varying temperature at two fixed pressures [Fig. 1(a)] and by varying pressure at four different temperatures [Fig. 1(b)]. Moreover, the variation of the volume $\Delta V(T,P)$ (Fig. 2) was measured over a wide range of temperature and pressure to determine the thermal expansivity properties for PPGE. Experimental details can be found in [7,21]. This allowed to independently estimate some of the parameters in Eq. (5) and to make our test more stringent.

From the analysis of the derivative of τ with respect to the temperature (reported elsewhere [22]) it was found that at atmospheric pressure τ shows a change of dynamics at a temperature $T_B\sim305$ K, below which the VFT equation applies [23]. Therefore in the following, for the analysis of the measurement at atmospheric pressure, only the data in the range 260–301 K were considered.

The structural relaxation time τ as a function of the reciprocal of temperature is shown in Fig. 1(a) for two isobaric measurements ($P=0.1$ MPa and 95.5 MPa). By the best fit of the data at atmospheric pressure ($P\sim0$) obtained by using Eq. (2) [solid line in Fig. 1(a)], it was found $A=DT_o=1634\pm26$ K, $T_o=217.4\pm0.4$ K, and $\log(1/\tau_o[s])=15.08\pm0.1$.

The structural relaxation time as a function of the pressure is shown in Fig. 1(b) for four isothermal measurements ($T=303.4$ K, $T=293.5$ K, $T=283$ K, and $T=274.5$ K).

From the analysis of the $\Delta V(T,P)$ data we determined: $\alpha(P=0.1\text{ MPa})=(5.8\pm0.1)10^{-4}\text{ K}^{-1}$, $b_1=1040\pm1$ MPa, $b_2=(4.15\pm0.03)10^{-3}\text{ K}^{-1}$, and $C=(9.1\pm0.2)10^{-2}$. By using these values we estimated the parameter $\gamma=(1.4\pm0.03)10^{-1}$ and $B(T)=1040\times\exp(-T\times4.15\times10^{-3})$ MPa. Moreover, in the analysis of the isothermal data the parameters T_o and A were fixed at the values estimated by the best fit at atmospheric pressure, while the parameter $\log(1/\tau_o)$ was adjusted within the estimated error (determined by the best fit at atmospheric pressure) so that the values for $P=0$ coincided with the data at $P=0$ of the isothermal measurement.

TABLE I. Best fit parameters obtained by using Eq. (2) with T_o substituted by T_o^* [Eq. (5)] to fit the structural relaxation time of PPGE for two isobaric measurement and four isothermal measurements. The second column reports $A=\mathrm{DT}_o$. As discussed in the text the parameters $b_1=1040$ MPa, $b_2=4.15\times10^{-4}\text{ K}^{-1}$, and $\gamma=0.14$ were independently determined from the thermal expansivity data.

T and P range	A [K]	T_o[K]	$-\log_{10}(\tau_o[s])$	β	δ/S_∞ [MPa^{-1}]	B[MPa]
$260\div301$ K at 0.1 MPa	1634 ± 26	217.4 ± 0.4	15.1 ± 0.1			
$0.1\div270$ MPa at 303.4 K	1634	217.4	15.04	1.24 ± 0.02	$(5.2\pm0.1)\times10^{-4}$	295.7
$1\div200$ MPa at 293 K	1634	217.4	15.08	1.19 ± 0.03	$(5.3\pm0.2)\times10^{-4}$	308.2
$4.2\div128$ MPa at 283 K	1634	217.4	15.03	1.18 ± 0.08	$(5.3\pm0.4)\times10^{-4}$	321.3
$2.3\div76$ MPa at 274.5 K	1634	217.4	14.9	1.1 ± 0.2	$(6.2\pm1)\times10^{-4}$	334.9
$279\div312$ K at 95.5 MPa	1627 ± 8	217.4	14.9 ± 0.1	1.2	5.2×10^{-4}	306
$279\div312$ K at 95.5 MPa	1623 ± 8	217.4	14.9 ± 0.1	1.2	5.2×10^{-4}	$b_1\exp(-b_2T)$

In conclusion, to fit the isothermal data of $\tau(T,P)$, only β and δ/S_∞ were free parameters. The best fit parameters for the different temperatures are reported in Table I, while the best fit are shown in Fig. 1(b) (solid lines). The values of β and δ/S_∞, estimated from the best fits of the four set of data, coincide within the error. Moreover, the estimated values are in agreement with what was expected from the physical properties of PPGE. In fact, substituting the best fit parameters and using $V^{melt}(T,0)=2.9\times10^{-4}$ m^3 mol^{-1} at $T=298$ K we calculated $S_\infty=211\pm4$ J K^{-1} mol^{-1} and $\Delta(\partial V/\partial T)=(1.31\pm0.04)\times10^{-7}$ m^3 K^{-1} mol^{-1}, respectively. The value of S_∞ results very close to that found for other glass formers [3], while the value for $\Delta(\partial V/\partial T)$ is very reasonable considering that $(\partial V^{melt}/\partial T)=\alpha V^{melt}(T,0)=(1.68\pm0.03)\times10^{-7}$ m^3 K^{-1} mol^{-1} at $T=298$ K.

Finally, the best fit of the isobaric measurement [solid line in Fig. 1(a)] was obtained by fixing the parameters T_o, β, and δ/S_∞ (using the average of the values estimated by the best fit) and the calculated value for γ and $B(T)=b_1\exp(-b_2T)$ from the thermal expansivity data. The parameters estimated from the best fit (Table I) of the isobaric measurement at 95.5 MPa resulted in agreement with those at atmospheric pressure. To estimate how the temperature dependence of $B(T)$ affects our results, the previous analysis was repeated in the same conditions by simply considering an average value for $B(T)$, instead of including its temperature dependence in the fitting function. By comparing the parameters estimated from this best fit (see Table I), only a small difference, within the error, on the parameter A can be observed (a plot of this second best fit is not reported, because not distinguishable from the previous one). Hence, as expected, the temperature dependence of the parameter $B(T)$ in the investigated range does not induce any appreciable deviation from a VFT behavior for isobaric measurements.

In conclusion, from our test of the modified AG model on six different sets of data we found that the model gives a good description of both pressure and temperature behavior of $\tau(T,P)$ over a wide investigated range by means of a single equation (and therefore of an unique set of fitting parameters). Moreover, here we have shown how some of the parameters [γ and $B(T)$] can be calculated by a direct measure of the pressure and temperature dependence of the molar volume $V(T,P)$. The other parameters estimated by the best fit of the $\tau(T,P)$ reasonably agree with the values expected from the physical properties of the material. Ergo, the present extension of the Adam-Gibbs theory seems suitable to describe both the temperature and pressure behavior of the structural relaxation time.

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