

Influence of temperature and pressure on dielectric relaxation in a supercooled epoxy resin

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Isothermal and isobaric dielectric measurements of a supercooled epoxy resin have been compared. A simple scaling relates isobaric and isothermal spectra corresponding to the same frequency of the main loss peak. Thus, the main and secondary processes retain a relative weight that is the same under isothermal and isobaric conditions. It is inferred that both pressure and temperature, equivalently, are able to take effect on the relaxation processes, without changing the relaxation mechanism itself. Careful analysis of the structural relaxation time behavior revealed that the traditional free volume equation, where only the macroscopic volume controls the pressure evolution of free volume, is not a suitable description of the data, as well as a Vogel-Fulcher (VF) type pressure dependent function. Based on a derivative method, a different function for describing the bidimensional surface $\tau(T,P)$ has been proposed, which accounts for the observed behavior through a nonlinear correction of the critical temperature T_0 in the VF law. The function we propose predicts pressure dependencies of the glass transition temperature and fragility which are appealing in view of a comparison with experimental results in this and many other systems. Interesting hints for interpreting the phenomenological results can be obtained within the Adam-Gibbs theory. [S1063-651X(99)09610-5]

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I. INTRODUCTION

Many fluids turn into glasses when cooled at sufficiently high rates. In the glassy state the system appears frozen in an amorphous phase conventionally characterized by values of viscosity exceeding 10^{13} Poise, typical of the solid state, corresponding to dielectric relaxation times longer than 10^2 s. A similar phenomenon occurs in liquids in which the molecular motions are slowed down as the result of an increase of pressure, and several features of the temperature-dependent response are recognized in the pressure-dependent response of glass-forming systems.

Compared to the great number of investigations carried out under varying temperature, little work has been done so far under varying pressure, and the similarities between the behaviors observed by cooling the systems and those which occur under compression have not been completely explored. In particular, experiments yielding full information on the relaxation spectrum as a function of pressure are rare, and only a few experimental papers are available which analyze the influence of pressure on the shape of dielectric spectra [1–4]. The natural question of whether differences in the relaxation dynamics exist on approaching the glass transition via isobaric cooling or isothermal compression arises.

One of the basic problems concerning the relaxation behavior in the supercooled state is finding a universal description of it. As regards the temperature dependence of the

structural relaxation time, the empirical Vogel-Fulcher equation provides a suitable representation for most glass-forming liquids over a wide dynamic range. Similarly, an attempt at finding a relation that describes the pressure dependence of the relaxation time for as wide as possible class of glass-forming systems seems to be in general justified. In this connection, many efforts in the past were made on the basis of a free-volume approach [5–8]; the outcomes were somewhat ambiguous, leading both to claims of validity of free-volume descriptions [7,8] and to indications of their failure [6,9]. Of some appeal was the expectation of a VF-like dependence on pressure [3,10]. An alternative approach that has given a physical explanation to the temperature dependence of the relaxation behavior in glass-forming liquids is provided by the Adam-Gibbs theory [11], based on the concept of configurational entropy earlier discussed by the theory of Gibbs and DiMarzio [12]. An extension of this last theory to incorporate the effects of pressure was developed [13], although it does not provide an explicit pressure-dependent function for the relaxation time. At present, the search for an appropriate description of the relaxation times with pressure is still partially entrusted to a phenomenological approach.

The aim of this paper is to study the isothermal and isobaric dielectric response of a fragile glass former (Epon828), in order to compare the relaxation dynamics under cooling or compression and to investigate the relaxation time vs pressure relationship. Epon828 is a highly pressure-sensitive system, relatively moderate pressure changes being able to induce significant changes of the structural relaxation time. This work exploits isothermal dielectric measurements car-

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ried out in a wide pressure range, and previous dielectric studies on the thermal vitrification of the same compound [14]. The contribution of the secondary relaxation process, which strongly affects the relaxation spectra, is taken into account, and great care is devoted to the extraction of the structural relaxation time data in view of being able to distinguish among different fit models and looking for a unified temperature-pressure description.

II. EXPERIMENT

Dielectric measurements of the commercial grade compound diglycidyl ether of bisphenol-A (Epon828 by Shell Co., equivalent epoxy weight ~ 190) were performed in a previous experiment at atmospheric pressure in the frequency range $10^2 - 2 \times 10^{10}$ Hz for temperatures from 163 to 353 K [14]. Measurements by changing the pressure from 0.1 up to 235 MPa were carried out on the same compound in the frequency range $10^{-2} - 10^7$ Hz at the fixed temperature of 293 K.

For isobaric dielectric measurements the impedance analyzer HP4194A and two network analyzers, HP8753A and HP8720C, were employed. In the lower frequency range, up to 40 MHz, a stainless steel cylindrical capacitor cell (empty cell capacitance, $C_0 \cong 2.4$ pF) was used. In the higher frequency range, up to 20 GHz, the scattering parameters of a transmission coaxial line ended by a cell ($C_0 \cong 0.3$ pF) in the infinite sample configuration were measured. The sample temperature was controlled by an electronic proportional controller using a heated dry nitrogen flux. Details about the experimental setup are reported elsewhere [15].

For isothermal high-pressure dielectric measurements the frequency response analyzer Solartron SI-1260 and the impedance analyzer HP4192A were employed. In this case a parallel stainless steel plates capacitor was used ($C_0 \cong 9.6$ pF). The pressure was measured by a Nowa Swiss tensometric pressure meter, and the temperature was controlled by means of a liquid flow provided by a thermostatic bath. More detailed description of the experimental setup with the diagram of the high-pressure dielectric cell can be found in Refs. [3,16].

In all experimental arrangements the sample was preserved from the contact with external agents. The temperature of the sample was stabilized within 0.1 K, while in isothermal experiment the pressure was stabilized within 0.3 MPa. Different measurement runs, separated from each other by long time intervals, turned out to be consistent. The glass transition temperature of Epon828 as dielectrically determined [14] was $T_g = 257$ K.

III. RESULTS

The dielectric loss factor ε'' , as a function of frequency, of Epon828 under atmospheric pressure at different temperatures is plotted in Fig. 1(a). The isothermal ε'' spectra of the same sample are drawn in Fig. 1(b) at the fixed temperature $T = 293$ K for different pressures. The presence of a main (structural or α) and a secondary (γ , see Ref. [14]) relaxation process is clearly shown in the isobaric spectra [Fig. 1(a)]. As discussed in a previous paper [14], the α - and γ -relaxation times increase with decreasing temperature ac-

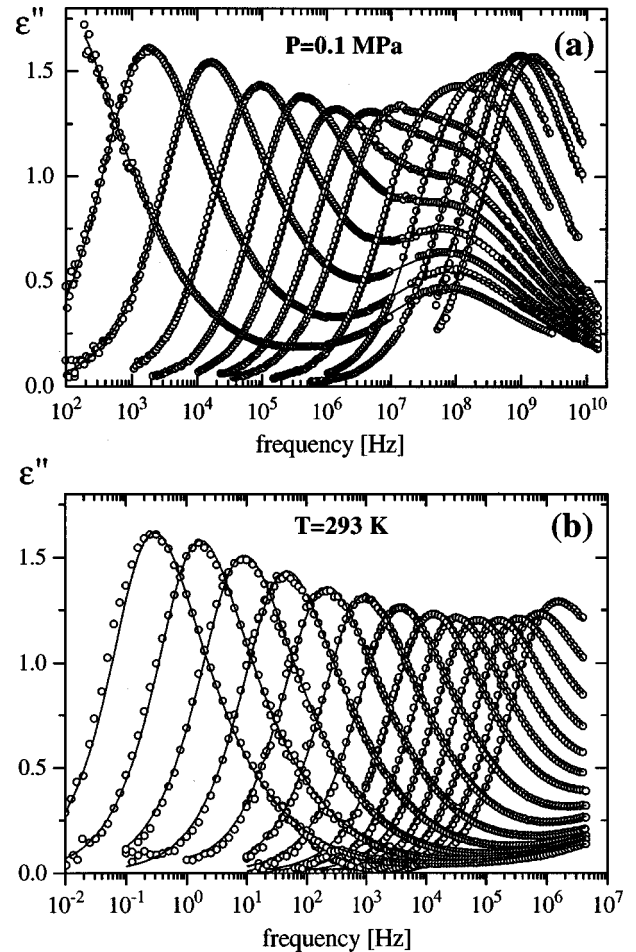


FIG. 1. (a) Dielectric loss factor ε'' of Epon828 at 0.1 MPa; the temperatures of the spectra are the following (from the left side): 268, 273, 278, 283, 288, 293, 298, 303, 313, 323, 333, 343, 353 K. Solid lines represent the fitting Eq. (1). (b) Dielectric loss factor ε'' of Epon828 at 293 K; the pressures of the spectra are the following (from the right side): 0.1, 14.9, 30.1, 45.2, 60.4, 75.2, 89.9, 109.7, 129.8, 150.1, 169.8, 190.1, 209.8, 230.5 MPa. Solid lines represent the fitting Eq. (1).

ording to the Vogel-Fulcher and the Arrhenius law, respectively. The presence of the two relaxations is again clearly visible in isothermal spectra [Fig. 1(b)]. By increasing the pressure the α -relaxation shifts towards lower frequencies, while the γ relaxation seems to be less sensitive to the pressure changes.

The secondary process is well distinguishable from the structural one in the isobaric spectra extending to GHz, while only its low frequency tail appears in the frequency window of the isothermal measurements. Anyway, the secondary relaxation strongly affects the dielectric response and its contribution was taken into account in the fitting procedure. Because of this, the spectra at different pressures were fitted by a superposition of two Havriliak-Negami (HN) functions

$$\varepsilon(\omega) - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_1)L_1(\omega) + (\varepsilon_1 - \varepsilon_\infty)L_2(\omega). \quad (1)$$

In this equation, $\varepsilon(\omega)$, ε_0 , and ε_∞ represent the complex dielectric permittivity and its low and high frequency limits, respectively, $\varepsilon_0 - \varepsilon_1$ and $\varepsilon_1 - \varepsilon_\infty$ are the main and secondary

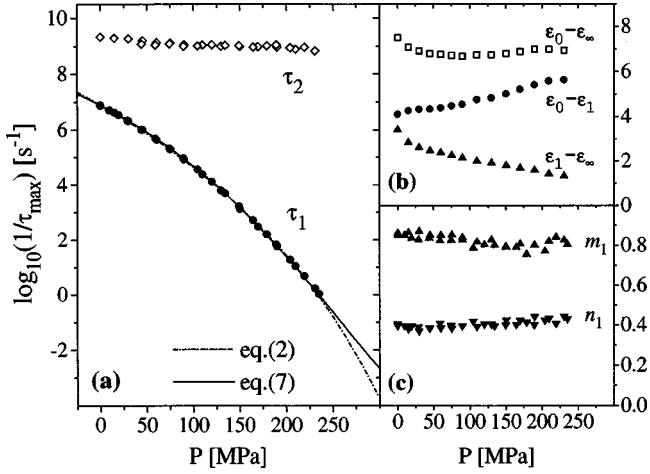


FIG. 2. (a) Main (τ_1 , solid circles) and secondary (τ_2 , open diamonds) relaxation time $\tau_{\max}=1/(2\pi f_{\max})$ vs pressure. The lines represent fitting equations as indicated in the legend (see text later). (b) The overall (squares), the main (circles), and the secondary (triangles) relaxation dielectric strengths vs pressure. (c) The shape parameters m_1 and n_1 vs pressure for the main relaxation.

dielectric strengths, $L(\omega)=[1+(i\omega\tau)^{1-\alpha}]^{-\beta}$ represents the normalized HN function, where the indexes 1 and 2 are referred to as the main and secondary relaxations, respectively. The fitting procedure was carried out on both ϵ' and ϵ'' data simultaneously.

The pressure change of the dielectric parameters is plotted in Figs. 2(a), 2(b), and 2(c). As a characteristic relaxation time we have chosen to report $\tau_{\max}=1/2\pi f_{\max}$ [Fig. 2(a)], corresponding to the frequency of the dielectric loss peak. When possible, τ_{\max} was determined from the spectra directly, otherwise it was analytically calculated from the HN fitting parameters. For the main relaxation the shape parameters $m=1-\alpha$ and $n=(1-\alpha)\beta$, describing the power law behavior of the dielectric loss in the low and high frequency limits respectively, do not appreciably change with pressure [Fig. 2(c)] and their values agree with those obtained from the isobaric spectra having an absorption peak falling into the same frequency range [14].

IV. DISCUSSION

A. Comparison between isobaric and isothermal spectra

The dielectric response of the system undergoing a temperature or pressure change, was analyzed by comparing isobaric and isothermal spectra having the main loss peak at the same frequency position. Apart from the spectra at 0.1 MPa and 293 K, which obviously coincide in the two sets of measurements, each isobaric ϵ'' spectrum is higher than the corresponding isothermal, but they superimpose very well when normalized to the value ϵ''_{\max} . From this result, shown in Fig. 3 for one representative couple of pressure-temperature values, some considerations can be drawn.

(i) Isobaric ϵ''_P and isothermal ϵ''_T loss spectra with the same frequency position of the α peak simply differ by a scaling factor S , i.e., $\epsilon''(\omega)_P=S\epsilon''(\omega)_T$. As the Kramers-Krönig equations imply that $S=[\epsilon'(\omega)-\epsilon_\infty]_P/[\epsilon'(\omega)-\epsilon_\infty]_T$, the corresponding ϵ' spectra are made coincident by the operation $[\epsilon'(\omega)-\epsilon_\infty]/\epsilon''(\omega_{\max})$, where ϵ'' is conveniently determined at the angular frequency of the loss peak ω_{\max} [Fig. 3(b)].

(ii) According to Eq. (1) each relaxation must independently fulfill the Kramers-Krönig relations. Consequently, as we observed that for the α relaxation is $\epsilon''_\alpha(\omega)_P=S\epsilon''_\alpha(\omega)_T$, the same scaling factor S has to be valid for the secondary relaxation. In particular, from the real parts of the permittivity we obtain $S=[\epsilon'_\alpha(\omega)-\epsilon_1]_P/[\epsilon'_\alpha(\omega)-\epsilon_1]_T=[\epsilon'_\beta(\omega)-\epsilon_\infty]_P/[\epsilon'_\beta(\omega)-\epsilon_\infty]_T$, which for $\omega=0$ becomes $S=(\epsilon_0-\epsilon_1)_P/(\epsilon_0-\epsilon_1)_T=(\epsilon_1-\epsilon_\infty)_P/(\epsilon_1-\epsilon_\infty)_T$, i.e., the scaling factor S is the ratio, in the isobaric and isothermal corresponding spectra, of both the main relaxation strengths and the secondary relaxation strengths.

(iii) The same relaxation time can be obtained by different couples of values of pressure and temperature, each of them corresponding to different values of the strengths. Considering that the change of the strength is related to the change of the density, this finding could be a straight consequence of the equation of state of the system. In this sense pressure and temperature would behave as equivalent thermodynamic variables for the relaxation of our supercooled sample and for the measurement ranges here considered. A different behavior was observed for phthalate derivatives in the super-

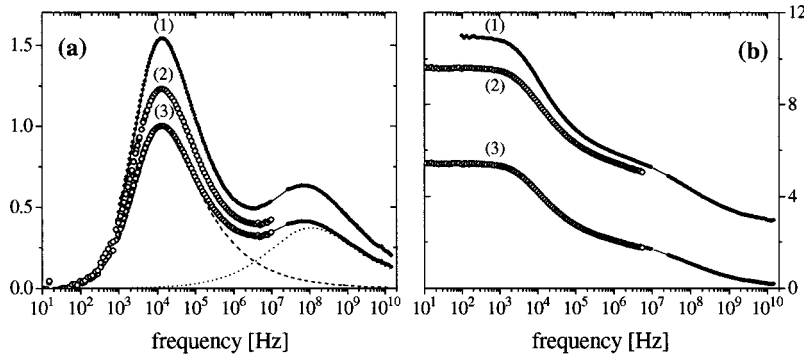


FIG. 3. (a) The ϵ'' spectrum labeled (1) was acquired at 277.5 K under atmospheric pressure; the ϵ'' spectrum labeled (2) was acquired at the pressure of 89.9 MPa at 293 K. The spectra labeled (3) are normalized to the value ϵ''_{\max} . The dashed and dotted lines represent the contributions to the normalized spectra of the main and secondary relaxations, respectively. (b) The ϵ' spectra labeled (1) and (2) are the isobaric and isothermal spectra, respectively, corresponding to the ϵ'' spectra in (a). The data labeled (3) represent the spectra normalized according to the ratio $(\epsilon' - \epsilon_\infty)/\epsilon''_{\max}$.

TABLE I. Results from the fit of τ_{max} for isobaric measurements at $P=0.1$ MPa and isothermal measurements at $T=293$ K. The parameters τ_0 , B_0 , and T_0 in the table are those obtained by fitting the VF law $\tau = -\tau_0\{B_0/[T-T_0]\}$, to the experimental data at atmospheric pressure: $\log_{10}(\tau_0) = 11.97 \pm 0.07$ s, $B_0 = 676 \pm 15$ K, $T_0 = 235.7 \pm 0.5$ s. K_0 and K'_0 are the isothermal bulk modulus and its pressure derivative, respectively, at atmospheric pressure. χ_r^2 is the reduced chi-square statistical variable.

Fit equation	Fitting parameters	χ_r^2
Eq. (2) $\tau = \tau_0 \exp\left\{\frac{BV_\infty}{V_0 - V_\infty} - \frac{BV_\infty}{V_0 - V_\infty} \ln(1 + \beta P)\right\}$ $\times [BV_\infty/(V_0 - V_\infty)]$ with $\alpha = 1 + K'_0$, $\beta = (1 + K'_0)/K_0$	$K_0(\text{fixed}) = 2.9$ GPa, $K'_0 = 9.3 \pm 2.7$, $B = 1.8 \pm 0.4$, $V_\infty = 0.760 \pm 0.009$ cm ³ /g	3.3
Eq. (4) $\tau = \tau_0 \exp\{B_0 P/(P_0 - P)\}$	$B_0 = 27.8 \pm 0.3$, $P_0 = 644 \pm 5$ MPa	3.4
Eq. (7) $\tau = \tau_0 \exp\{B_0/[T - (T_0 + bP + cP^2)]\}$	$b = (19.7 \pm 0.1) \times 10^{-2}$ MPa ⁻¹ K, $c = (-2.43 \pm 0.04)$ $\times 10^{-4}$ MPa ⁻² K	0.98

cooled state, where pressure seemed to increase the strength of the secondary relaxation more than the equivalent temperature change [4].

B. Pressure dependence of the structural relaxation time

In this section a more quantitative analysis of the pressure behavior of the structural relaxation time is reported, starting from the check of the $\tau(P)$ functions most frequently invoked in the literature. The next paragraph will be devoted to a more general approach, accounting for both the pressure and temperature dependences of the structural relaxation time.

Among many attempts to give a physical basis to the observed behavior of the relaxation time of systems in the amorphous phase, a simple picture is provided by the free-volume model [5,17], that lends itself to be applied both to isobaric and isothermal conditions. According to this model, the dependence of the relaxation time τ on free-volume has often been expressed as

$$\frac{\tau}{\tau_0} = \exp\left(\frac{BV_\infty}{V - V_\infty} - \frac{BV_\infty}{V_0 - V_\infty}\right), \quad (2)$$

where V is the volume of the fluid and $V - V_\infty$ is the free-volume, V_∞ being a limiting molecular volume whose physical meaning is still debated [7,8]; τ_0 and V_0 are the quantities in a reference condition. Using the Tait equation of state to represent the $V(P)$ relationship [18], $V = V_0[1 - (1/\alpha)\ln(1 + \beta P)]$ with $\alpha = 1 + K'_0$ and $\beta = (1 + K'_0)/K_0$ being, respectively, K_0 and K'_0 the isothermal bulk modulus and its pressure derivative at zero (\sim atmospheric) pressure, Eq. (2) can be considered to describe the isothermal pressure dependence of the relaxation time. To fit the isothermal data of Fig. 2(a) we used the value of τ_0 at atmospheric pressure, while the volume $V_0 = 0.8554$ cm³/g was deduced from the density $\rho = 1.169$ g/cm³ at 293 K. The isothermal bulk modulus $K_0 = 2.9$ GPa at 293 K was valued from the relaxed longitudinal acoustic velocity c_0 measured by an ultrasonic technique [19], using the relation

$$K_0 = \frac{\rho c_0^2}{1 + \rho c_0^2 \lambda^2 T V / C_p}, \quad (3)$$

where λ is the thermal expansion coefficient and C_p the isobaric specific heat [20]. The best values of the adjustable parameters B , V_∞ , and K'_0 , were (Table I) $B = 1.8 \pm 0.4$,

$V_\infty = 0.760 \pm 0.009$ cm³/g, $K'_0 = 9.3 \pm 2.7$. The resulting free-volume parameters seem to be quite acceptable and similar to that found in free-volume descriptions of viscosity data for several materials [8,9]. In particular, the value of B is consistent with that ($0.5 \leq B \leq 1.5$) considered as physically meaningful in the model of Cohen and Turnbull [17], and the value of the fractional free volume $(V - V_\infty)/V \approx 0.11$ is reasonable. In spite of the good appearance of the fitting curve in the Arrhenius-plot [dash-dot line in Fig. 2(a)], the value of the reduced chi-square, 3.3, clearly indicates that the deviation from the experimental data is well beyond the experimental errors. This provides evidence that the free-volume equation in the form (2) takes the essential features of the pressure behavior of τ , but it is not suitable for a rigorous description over a wide pressure range.

The analogies observed in the response of glass-forming liquids when temperature is decreased or pressure is increased, have driven some authors (see Ref. [21], and references therein) to describe empirically the rapid increase of the structural relaxation time with pressure in isothermal measurements by simply replacing temperature with pressure into the phenomenological VF law

$$\tau = \tau_0 \exp\left\{\frac{B_0 P}{P_0 - P}\right\}, \quad (4)$$

where P_0 is the limit pressure where τ diverges, B_0 is a constant, and τ_0 is the relaxation time measured in the low-pressure (\sim atmospheric) limit. The precision of the τ values (the relative error is between 1.5 and 3 %) allowed to analyze our data by applying the derivative analysis [22], which is more sensitive to changes of the functional dependence. Accordingly, the quantity $\Phi_P = [-d \log_{10}(1/\tau)/dP]^{-1/2}$ was numerically calculated and plotted as a function of P (Fig. 4). As in this representation a linear behavior of Φ_P vs P corresponds to a VF-like behavior of τ vs P , it is apparent that the structural relaxation time does not comply with a pressure-VF behavior over the whole pressure range investigated (dashed line; see parameters in Table I). A linear fit of the data in Fig. 4 is acceptable within the experimental errors up to pressures not higher than ~ 150 MPa, so that a VF-like description covers only four of the seven decades of τ spanned by the data. On the contrary, the temperature dependent data do not show any deviation from VF behavior in the same τ region [23]. The failure of Eq. (4) in the case of Epon828 disagrees with conclusions reported in previous works [3,4,10,21], where the pressure-VF law was consid-

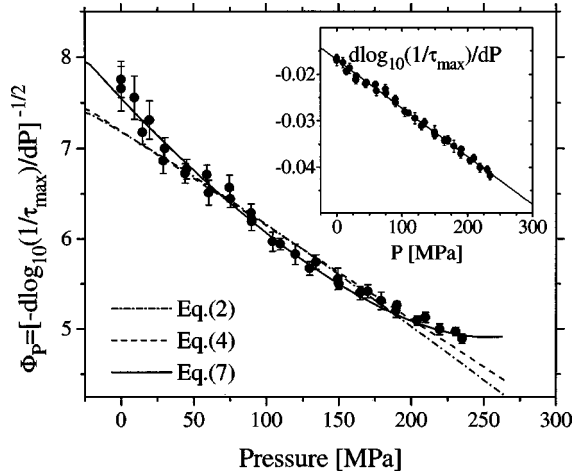


FIG. 4. The quantity $\Phi_P = [-d \log_{10}(1/\tau_{\max})/dP]^{-1/2}$ vs pressure at 293 K. The lines represent fitting equations as indicated in the legend. (Inset): pressure derivative of $\log_{10}(1/\tau_{\max})$ vs pressure at 293 K. The straight line represents a second order polynomial function.

ered a satisfactory representation of the experimental behavior for several glass-formers. However, Fig. 4 indicates that the deviation from Eq. (4) is appreciable only at enough high pressures and it becomes apparent only if the data analysis is performed in the Φ - P plane. The fitting free volume equation [Eq. (2)] is also drawn in Fig. 4 as a dash-dot line. The clear deviation from the experimental points confirms the high value of the reduced chi-square. Incidentally, we note that, although it remains an essentially empirical law, the VF-like equation has been also derived within a free volume approach [3,6].

The derivative path followed to test Eq. (4) shows that the values of the log-derivative of $1/\tau$ have linear correlation coefficient 0.997, thus suggesting the possibility to use a second order polynomial function $\log_{10}(1/\tau) = a_0 + a_1P + a_2P^2$ (straight line in inset of Fig. 4). This function contains the same number of free parameters as the VF-like one, but the reduced chi-square is close to unit (0.97). To date no explanation of such description has yet been proposed, though other authors, by close inspection of dielectric relaxation times in polypropylene glycol [24] and viscosity data in orthoterphenyl and salol [9], pointed out that parabolic expressions provide excellent phenomenological parametrizations of experimental data for different isotherms as well.

C. Temperature-pressure dependence of the structural relaxation time

A more general approach for describing the change of the relaxation time can be attempted, taking into account for both pressure and temperature dependence. Any effort in that direction has to face up to the well-established result that the VF equation is able to describe the change of the relaxation time over a wide temperature range for a large number of glass forming systems [25]; in particular, such description is quite appropriate for our system over more than eight decades of τ , including the dynamic range covered by the pressure-dependent measurements [14,23]. As a consequence, the most natural approach is to incorporate the effect

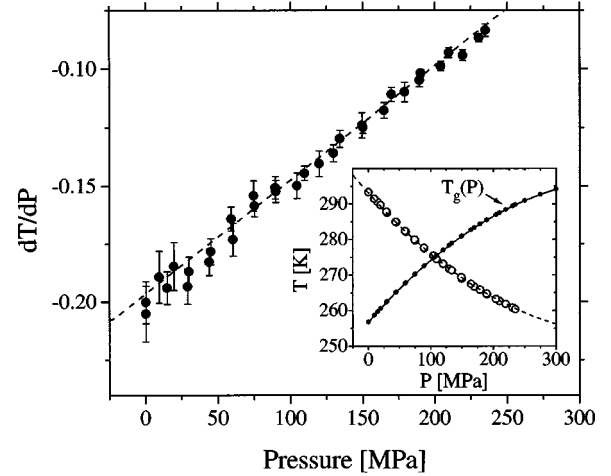


FIG. 5. Derivative with respect to the pressure of the temperature in isobaric measurements corresponding to the same value of τ_{\max} in isothermal measurements. The experimental data used to calculate this derivative are shown in the inset. The dashed line is the best fit obtained by a linear regression. (Inset): open circles represent couples of temperature and pressure values corresponding to the same value of τ_{\max} in isobaric and isothermal measurements, respectively. The error bars are smaller than the symbol size. The dashed line is the best fit obtained by a second order polynomial regression according to Eq. (6). The pressure behavior of the glass transition temperature, $T_g(P)$, predicted by using Eq. (7), is reported on this plot by full points.

of pressure in the usual VF law assuming some pressure dependence of its parameters, as already tried in various previous studies [6,26,27] and in general expressed by the following equation:

$$\tau(T, P) = \tau_0 \exp\left\{\frac{B_0(P)}{T - T_0(P)}\right\}, \quad (5)$$

where in the first place the effect of pressure is considered for B_0 and T_0 , which are in the exponential argument, and neglected for the pre-exponential factor τ_0 [26,27]. In the following, to come to an appropriate form of Eq. (5), the indication given by the isobaric and isothermal sections of the bidimensional surface $\tau(T, P)$ will be joined with the observation of recurrent empirical behaviors and some physical considerations.

Concerning the bidimensional surface $\tau(T, P)$, both the isothermal section $\tau(T_m, P)$ at the measurement temperature $T_m = 293$ K and the isobaric section $\tau(T, P_m)$ at $P_m = 0.1$ MPa are monotonous functions, therefore a one-value transformation $T(P)$ must exist such as $\tau(T_m, P) = \tau[T(P), P_m]$. The $T(P)$ function can be experimentally obtained by considering the couples of temperature-pressure values corresponding to the spectra with the same structural relaxation time for the isobaric and isothermal measurements, respectively (inset of Fig. 5). An inspection of the derivative dT/dP (Fig. 5), numerically calculated from the data in inset of Fig. 5, reveals an almost linear trend (the linear correlation coefficient is 0.997). This behavior supports with good accuracy a quadratic $T(P)$ dependence

$$T(P) = T_m - bP - cP^2. \quad (6)$$

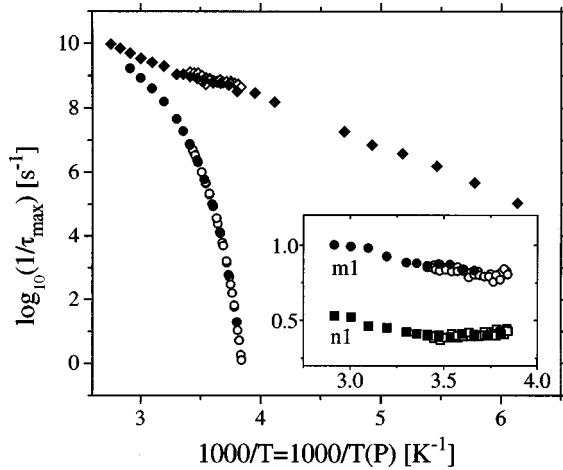


FIG. 6. The main and the secondary relaxation times under isobaric (full symbols) and isothermal (open symbols) conditions, reported on the same scale according to the correspondence shown in inset of Fig. 5. In the inset: the same rescaling is shown for the shape parameters m_1 and n_1 of the main relaxation.

Incidentally, the best-fitting function according to Eq. (6) (dashed line in inset of Fig. 5) can be used to transform the data from pressure to temperature domain (Fig. 6). This gives a different way to observe the results drawn in Sec. IV A and shown in Fig. 3: after the pressures are rescaled, the superposition of both isobaric and isothermal relaxation times and shape parameters for the main relaxation can be observed. In particular, Fig. 6 shows up the equivalent temperature range covered by the pressure measurements.

Replacing Eq. (6) in $\tau(T, P_m) = \tau_0 \exp[B_0/(T - T_0)]$, yields $\tau(T_m, P) = \tau_0 \exp[B_0/(T_m - T_0 - bP - cP^2)]$. This result suggests that in Eq. (5) $B_0(P)$ may be a constant and $T_0(P)$ a quadratically pressure-dependent parameter according to

$$\tau(T, P) = \tau_0 \exp\left\{\frac{B_0}{T - (T_0 + b'P + c'P^2)}\right\}, \quad (7)$$

where b and c are constant. It is worth stressing that Eq. (7) is specially suitable for representing our pressure dependent data, as shown in Fig. 4 by the solid line obtained by a fitting procedure giving the parameters $b = (19.7 \pm 0.1)10^{-2} \text{ MPa}^{-1} \text{ K}$ and $c = (-2.43 \pm 0.04)10^{-4} \text{ MPa}^{-2} \text{ K}$. The value of the reduced chi-square for this fit is 0.98 (Table I).

As a further support of the reliability of Eq. (7), we compare its predictions with the observed pressure change of some quantities which play an important role in defining the behavior of glass-forming liquids, such as the glass transition temperature T_g and the fragility parameter. Taking $T = T_g$ in correspondence of $\tau = 10^2 \text{ s}$, T_g is predicted by Eq. (7) to increase with pressure according to a parabolic function with downward concavity, and $T_g(P) - T_0(P) = \text{const}$ (the predicted $T_g(P)$ for Epon828 is shown in inset of Fig. 5). A similar behavior is fairly well documented in the literature, where a nonlinear rise of T_g (or the closely related temperature T_0) with pressure has been reported for several glass-forming liquids. In particular, a marked deviation of T_g from linearity was experimentally recognized in some polymeric systems [13,28], in glycerol and dibutyl-phthalate [8] and, more recently, in polypropylene-glycol of two different mo-

lecular weights [24]. Temperature- and pressure-dependent studies of epoxy resins, different but very similar to Epon828 [10,29], have shown in a similar pressure range that a linear pressure dependence of T_g can be applied only in the first approximation and that deviations from linearity are anyway detectable. If limited pressure ranges can obscure some non-linearity [26,27,30], the need of taking account of deviations from linear behavior seems to be a natural consequence of the investigation of wider pressure ranges.

The fragility parameter $D = B_0(P)/T_0(P)$ accounts for the departure from Arrhenius behavior on approaching the glass transition and is widely employed in classifying the glass-forming liquids as *strong* (high D) and *fragile* (low D) [31]. Concerning this parameter, Eq. (7) simply provides the expression $D(P) = B_0/(T_0 + bP + cP^2)$, which is a smoothly decreasing function in a wide pressure range and then eventually increasing. The study of pressure effects on fragility is of recent interest, and the available data generally do not reach very high pressures. However, the experimental database seems to indicate a general tendency of fragility to increase (of D to decrease) with pressure, as implied by Eq. (7). In particular, a considerable increase of fragility in the intermediately strong glycerol [8], and a small but significant change toward a higher degree of fragility in polypropylene-glycol [24] have been found. Also the somewhat complicated behavior observed in a recent viscometry study of salol [9] for the index $m = \partial \log_{10} \tau / \partial (T_g/T)|_{T=T_g}$, implying a minimum in the fragility parameter D , could be described by means of Eq. (7). It is worth noting that the findings that fragility of methanol over a limited pressure range [32], orthoterphenyl [9], dibutyl-phthalate [8], and epoxy resins [10,29] is almost pressure independent within the experimental errors can also be accounted for by this equation. The values of the fitting parameters b and c can be reflected, indeed, in a change of D that is within the experimental error. This is proved in the case of Epon828, where only a change of D from 2.9 to 2.5 is predicted when the pressure is increased up to 235 MPa. Some suggestion that fragility does not really change appreciably with pressure in our system could be inferred from the shape of the main relaxation which is almost invariant under temperature and pressure changes. Böhmer *et al.* [33] found a correlation between the shape and the fragility parameter. If that holds for Epon828, one should expect that fragility is approximately constant and Eq. (7) is suitable to represent our data.

Really, since the relaxation times of Epon828 are compatible with a constant fragility they do not allow us to exclude the description provided by Eq. (5) with the parametrization $B_0(P) = DT_0(P)$, where D is constant and $T_0(P)$ is a quadratically pressure-dependent parameter (the fit gives a reduced chi-square of 0.99). Some distinction from Eq. (7) would become possible at higher pressures only. Anyway, we think that the possibility that pressure affects the fragility may be in general physically more realistic. In fact, a relation between the deviation from Arrhenius behavior and the degree of cooperativity in the molecular motion is generally thought, and it is connected with the topological features of the potential energy hypersurface characteristic of systems of different bonding character [31], and with the fluctuation ΔN_c of the coordination number of the molecules in the fluid [34]. In this view, strong liquids, which are structurally char-

acterized by highly directional bonds and a well-defined network coordination, have a relatively small density of minima on the energy surface and a small ΔN_c , while fragile liquids, with nondirectional or weakly directional bonds, are characterized by a high density of accessible minima and a greater ΔN_c . Under compression the atoms are driven closer together, and it is plausible to expect a change in fragility. The possibility of such a change is supported by the previously mentioned experimental evidence obtained in different glass-forming systems [8,9,24].

Pressure dependencies of B_0 and T_0 different from that here proposed have been considered in the literature: B_0 constant and $T_0(P)$ linearly dependent on pressure were employed to get an equation suitable for fitting conductivity data of molten salts under pressure over a very limited conductivity range [27]. Starting from a free-volume approach, a linear dependence on pressure of both $B_0(P)$ and $T_0(P)$ was tested to describe the relaxation times obtained by photocorrelation, specific heat, and dielectric spectroscopy of supercooled orthoterphenyl, proved to be unsuccessful (Ref. [6], and references therein). In a later study of epoxy resin [10], such a linear behavior of both $B_0(P)$ and $T_0(P)$ was verified in first approximation. A more careful analysis reveals that also those data can be better described by means of a quadratic pressure dependence of $T_0(P)$ and a constant B_0 as expressed by Eq. (7). On the other hand, it must be noticed that linear parametrizations of $B_0(P)$ and $T_0(P)$ just give a VF-like pressure dependence of τ for any fixed temperature, together with a linear behavior of T_g with pressure, which are not suitable for fitting the data in the present and many other cases [8,10,13,24,28,29].

The pressure dependence of B_0 is quite possible, but the present results indicate that this dependence is at worst rather weak, and it can be considered as a higher correction than that given by the second-order term in T_0 . The need to regard the influence of pressure on T_0 as overwhelming the effect on B_0 can be supported by those theories that drive to focus on T_0 as a basic parameter in the interpretation of the liquid-glass transition [11,12]. If the critical temperature T_0 in the empirical VF equation is identified [31], or in any case closely related, with the transition temperature where, according to the equilibrium theory of Gibbs-DiMarzio [12], the configurational entropy vanishes, then it is reasonable to think a significant influence of pressure on this latter temperature does exist. A proof is given by the statistical model for amorphous polymers by Gibbs-DiMarzio, extended to incorporate the effects of pressure [13], that also provides a basis to consider nonlinear increases with pressure of the transition temperature. In fact, the extended theory, though not providing an explicit expression of it, also predicts that the transition temperature where the configurational entropy is proved to vanish should deviate from linearity under pressure, initially increasing and eventually approaching a finite asymptote at very high pressures. A similar behavior is well parametrized for not too high pressures by a simple quadratic correction of T_0 with downward concavity, as that included in Eq. (7).

Furthermore, in the molecular-kinetic treatment of Adam-Gibbs [11], where the transition probabilities of cooperative rearrangements in the glass-forming liquid are determined by

the size of the cooperatively rearranging region, the relaxation time is related to the configurational entropy of the melt through the expression

$$\tau = \tau_0 \exp(C/TS_c), \quad (8)$$

where S_c is the configurational entropy, which reflects the number of potential energy minima in the hypersurface which are accessible to the system, and C contains a potential energy $\Delta\mu$, hindering the cooperative rearrangements. The configurational entropy can be developed in terms of the transition temperature and of the difference in specific heat ΔC_p , between the melt and the glass at the transition. Likewise the dependence on temperature [11], it is reasonable that in first approximation the dependence on pressure of $\Delta\mu$ and ΔC_p can be neglected. This is qualitatively confirmed by the pressure invariance of the shape parameters [see Fig. 2(c)], whose values can be related to the extent of intermolecular and intramolecular interactions [35]. From these considerations it can be inferred that a pressure dependence of the temperature of vanishing configurational entropy, i.e., T_0 , may be dominant with respect to that of the other parameters, i.e., B_0 .

As a final remark, we note that along the thermodynamic treatment of the liquid-glass transition, the change of T_0 with pressure has been shown [13] to satisfy the Ehrenfest relation valid for a second-order thermodynamic transition

$$dT_0/dP = T_0 V_{T_0} \Delta\alpha / \Delta C_p, \quad (9)$$

where V_{T_0} is the molar volume at T_0 , and $\Delta\alpha$ and ΔC_p are the differences in the thermal expansion coefficient and the heat capacity across the transition. According to Eq. (7) the parameter $b = 19.65 \times 10^{-2} \text{ MPa}^{-1} \text{ K}$ should give the right-hand side of Eq. (9) at $P=0$, and it can be used to predict the thermodynamic quantity ΔC_p at atmospheric pressure [36], which can experimentally be easily accessed by calorimetry. The value we expect is $\Delta C_p \approx 39.8 \text{ cal mol}^{-1} \text{ K}^{-1}$ or $0.11 \text{ cal g}^{-1} \text{ K}^{-1}$ that is a quite reasonable value.

V. CONCLUSIONS

In this paper the dielectric response of the epoxy resin Epon828 under isobaric and isothermal conditions has been compared over more than seven decades of relaxation times. The isobaric ε_p'' and isothermal ε_T'' loss spectra with the main loss peak at the same frequency position differ by the scaling factor $S = \varepsilon_{p, \max}'' / \varepsilon_{T, \max}'' = (\varepsilon_0 - \varepsilon_1)_p / (\varepsilon_0 - \varepsilon_1)_T = (\varepsilon_1 - \varepsilon_\infty)_p / (\varepsilon_1 - \varepsilon_\infty)_T$. This scaling behavior means that the main and secondary processes contribute to the overall relaxation with a relative weight which is the same under isothermal and isobaric conditions. Moreover, also the shape parameters, which describe the influence of intramolecular and intermolecular interactions [35], are the same, thus suggesting that relaxation processes with the same relaxation times are controlled by the same microscopic interactions, in spite of the different thermodynamic conditions. These findings could indicate that pressure and temperature behave as equivalent thermodynamic variables for the studied sample in the investigated range, and no appreciable difference in the molecular relaxation mechanism is involved on approaching the glass transition via isobaric or isothermal paths.

Concerning the structural relaxation time behavior, we have found that a free-volume equation in the form of Eq. (2) is not a satisfactory representation of the data. This observation agrees with recent results on viscosity data of orthoterphenyl [9], but disagrees with previous claims that such free-volume description is valid in very wide pressure ranges [8] up to the glass transition [7]. We note that according to Eq. (2) it is the macroscopic volume V that governs the pressure-induced variation of free-volume $V - V_\infty$, while there is no provision for a change of V_∞ . The inadequacy of Eq. (2) might be due to this crude representation of free-volume.

A deeper investigation has been performed by applying a derivative method that amplifies the dependence on pressure of relaxation times and eventually linearizes its trend. Clear evidence has been given of deviations from a VF-like pressure dependence, that has been frequently invoked on the basis of empirical observations or free-volume approaches. Guided by the results of the derivative analysis, a different function has been here proposed, accounting for both the pressure and temperature dependence of the structural relaxation time [Eq. (7)]. It retains the well-established VF law for the temperature-dependent behavior, which is proved to be verified in the dynamic range investigated, and incorporates the effects of pressure into the VF parameter $T_0(P)$. Equation (7) reveals remarkable features in view of its predictions for the evolution under pressure of the glass transition temperature and the fragility parameter. In particular, it accounts for an increasing or almost constant fragility, as recently recognized in several systems, and for nonlinear raise with pressure of the glass transition, as theoretically expected for sufficiently high pressures and confirmed by experimental findings. Equation (7) is also qualitatively supported by theoretical models that, ascribing the sluggish relaxation behavior governing the glass transition to a dearth of configurations, i.e., to a vanishing configurational entropy S_c , make it plausible to expect that pressure mainly influences the temperature where S_c vanishes, i.e., T_0 , rather than other physical parameters, connected with B_0 .

Our proposal, though arising from a phenomenological approach, could be a useful spur for further theoretical studies in this field. Moreover, singling out a more appropriate function for describing temperature and pressure-dependent relaxation times should be helpful to extract more reliable quantities when extrapolations of the experimental data are needed. It is known that the calculation of physical parameters connected with the relaxation time behavior is strongly altered by the use of different fitting functions [8,9,29].

The limited number of available experimental data still hinders an accurate check of Eq. (7). For this purpose more temperature and pressure dependent data are desirable, especially those extending at higher pressures, where the bending of $T_0(P)$ predicted by the Gibbs-DiMarzio theory should be more visible. A check of the predicted value ΔC_p could be an additional test of the suitability of a nonlinear $T_0(P)$ dependence, besides of the consistency with the underlying physical model.

On the whole, the analysis here proposed has developed a procedure able to distinguish between different functions less ambiguously than it was done in the past. It is clear that a deeper experimental investigation, involving a similar analysis on more glass-forming systems is still required, in order to have a more comprehensive view of pressure effects on dielectric spectra, as well as their comparison with temperature effects.

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- as $M'(\omega) = \rho c(\omega)^2$, where ρ is the density. In the static limit the relationship $M'(0) = \gamma K_0$ is valid, being K_0 the isothermal bulk modulus and γ the ratio of the isobaric to isochoric specific heats, so that the relation $\rho c_0^2 = \gamma K_0$ is obtained, between K_0 and the relaxed longitudinal acoustic velocity c_0 . Replacing γ via the Mayer relation, $\gamma = (1 - \lambda^2 K_0 T V / C_p)^{-1}$ with λ the thermal expansion coefficient and C_p the isobaric specific heat, Eq. (3) follows. Using the values at $T = 293$ K: $c_0 = 1.65 \times 10^3$ ms⁻¹ (from Ref. [19]), $\rho = 1.169$ g/cm³, $\lambda = 4.87 \times 10^{-4}$ K⁻¹ and $C_p = 1.88$ J g⁻¹ K⁻¹, Eq. (3) gives $K_0 = 2.9$ GPa for Epon828.
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