

Temperature and pressure dependence of the α relaxation and configurational entropy of a prototype glass former

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(Received 28 March 2002; published 16 September 2002)

The α relaxation process of the fragile glass former salol is investigated in the T - P domain by means of photon correlation spectroscopy. We find that a time-pressure superposition principle is obeyed for the relaxation function in addition to the time-temperature superposition. The behavior of the relaxation time is studied by using an extended version of the Adam-Gibbs model including the pressure dependence. The excellent conformity of the equation describing the bidimensional surface $\tau(T,P)$ to the experimental data provides a positive check for this model, here verified on photon correlation measurements. The same model gives a rationale of the phenomenological expressions recently introduced to describe the changes in the slow dynamics induced by varying both temperature and pressure. These findings suggest that the reduction of configurational entropy actually guides the liquid toward the glass transition.

DOI: 10.1103/PhysRevE.66.032501

PACS number(s): 64.70.Pf, 64.90.+b, 78.35.+c

The study of the dynamics of glass forming systems is of great importance for both basic and technological reasons. Indeed, the glass formation is crucial in the processing of food, in the technology of many daily used materials, from window glasses to polymers and composite materials, for the stabilization of biochemicals, for understanding structure and dynamics of proteins, etc. [1]. Although the molecular processes underlying the glass formation are not fully understood, the supercooling of liquids and the glass formation is known since the ancient age, showing two most significant common features: (i) the stretched-exponential shape of the α relaxation function and (ii) the steep increase of the α relaxation time τ approaching the glass transition.

The glass transition can be induced both by decreasing *temperature* and by increasing *pressure*, the first path being usually preferred due to the high pressure (of the order of MPa) required for inducing dynamical changes similar to those obtained within few tens of degrees changes of temperature. For this reason, the glass formation is widely studied by measuring the temperature behavior of the α relaxation function of supercooled liquids. On the other hand, relatively few studies of pressure dependence of the α relaxation have shown to give a deeper insight into the nature of the transition. The high-frequency dynamics under compression has been investigated by means of both light scattering [2] and incoherent neutron scattering [3] in order to test the mode coupling theory [4] and study the equation of state of liquids [5]. The low-frequency dynamics under pressure has been investigated by dielectric spectroscopy to study the time-pressure scaling law [6–8], and the fragility of different glass formers [9,10]. In the same low-frequency regime, photon correlation technique has been also used to test both the scaling of the α relaxation and the pressure dependence of fragility [11], showing the traces of some universal behavior. This phenomenological picture is still waiting for a comprehensive theoretical explanation.

A suggestive approach to the problem is nowadays given by the energy landscape framework that relates microscopic,

thermodynamic, and dynamic properties of supercooled liquids (see, for example, Refs. [1,12–15]). In this frame, configurational entropy is suggested to guide the dynamics close to the glass transition [16–18]. Consistent with this approach, a pressure extended Adam-Gibbs (PEAG) model has been recently proposed to account for both T and P variations of the α -relaxation time [19].

Here, we focus on the T and P behavior of the α -relaxation function of the prototypical glass former salol. The results of our investigation (i) show that a *time-temperature-pressure superposition principle* (TTPS) is obeyed for the α -relaxation function, extending to the pressure parameter the time-temperature superposition recently reinvestigated by Olsen *et al.* [20]; (ii) strongly support the validity of the PEAG model that is able to correctly represent the $\tau(T,P)$ behavior in the whole range investigated here. These findings, together with the ability of the PEAG model to give a rationale of the T and P phenomenology of highly viscous liquids, confirm the configurational entropy to be a key to the slow dynamics of glass forming systems.

We performed photon correlation spectroscopy (PCS) measurements under high hydrostatic pressure, up to 190 MPa, at different temperatures (namely, 267.1, 268.6, 271.0, 274.6, 278.3, and 280.4 K). Depolarized light scattering spectra (VH - 90° scattering geometry) were collected using an apparatus consisting of an Ar-ion laser, operating at 514.5 nm, a high pressure cell (a detailed description of the cell is reported in Ref. [21,22]), and an ALV5000E digital correlator. High pressure was generated by a Nova Swiss membrane compressor and measured by a Heise gauge having a resolution of 0.3 MPa. Nitrogen was used as pressure transmitting medium and temperature measured by a thermocouple with a typical error of 0.1 K. Salol [2-hydroxy benzoic acid phenyl ester, 2-(HO) C₆H₄CO₂C₆H₅] purchased from Aldrich company, purity 99%, was filtered (0.22- μ m Millipore filter) into a dust-free cylindrical cell of 10 mm o.d. at about 80 °C.

In Fig. 1, normalized homodyne correlation functions $[g^{(2)}(t) - 1]/B^2$, taken at 267.1 K in the 88–189.5 MPa

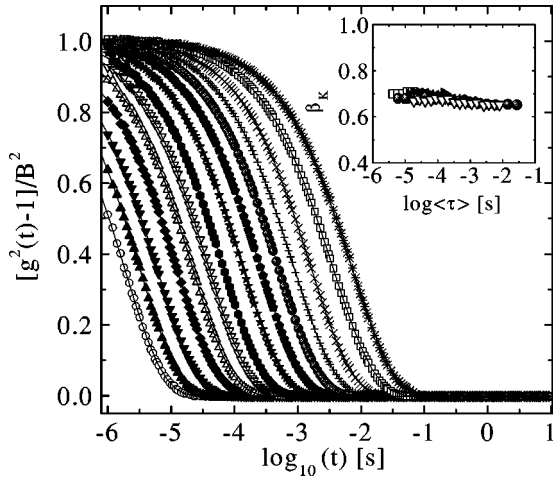


FIG. 1. Normalized photon correlation functions collected at a constant temperature of 267.1 K plotted as a function of $\log_{10}(t)$ [s]. Pressures from left to right are 88, 95, 102.5, 110.5, 119, 125, 132.5, 141, 148.5, 156.5, 163.5, 171, 181, and 189.5 MPa. The solid lines represent the fits to the data using the KWW function. The value of the stretching parameter β_K in the whole T - P range is plotted in the inset as a function of $\log_{10}(\tau)$.

pressure range are shown. Spectra were fitted using the Kohlrausch-Williams-Watt (KWW) [23] formula through the equation [24]

$$g^{(2)}(t) - 1 = [B \exp(-(t/\tau_K)^{\beta_K})]^2. \quad (1)$$

The values of the relaxation time τ_K and of the stretching parameter β_K were used to calculate the average relaxation time $\langle \tau \rangle$ by using the formula $\langle \tau \rangle = \tau_K / \beta_K \Gamma(1/\beta_K)$, where Γ is the gamma function. The values of $\langle \tau \rangle$ as a function of pressure at different temperatures are reported as symbols in

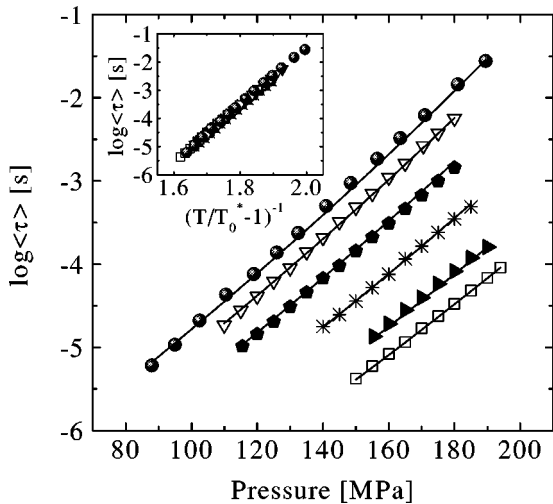


FIG. 2. Isothermal data for average relaxation times (symbols), $\log_{10}(\tau)$ [s], compared with best-fit calculated curves using the pressure extended Adam-Gibbs (PEAG) model (solid lines). Temperatures from top to bottom are 267.1, 268.6, 271.0, 274.6, 278.3, and 280.4 K. In the inset, the master plot of $\tau(T, P)$ as a function of the reduced temperature is shown.

Fig. 2. The values of β_K (0.68 ± 0.02) are almost T and P independent. This is evident in the inset of Fig. 1 where the stretching parameter, evaluated at several pressures and temperatures, is plotted in the whole time regime investigated. Recalling the relationship between the parameters β_K of a KWW function and β_{CD} of a Cole-Davidson (CD) function [25], we obtain $\beta_{CD} = (0.55 \pm 0.02)$, consistent with the $\omega^{-1/2}$ high-frequency α behavior generally found for those systems where the time-temperature superposition applies [20]. We note that the present result of a T and P independent $\omega^{-1/2}$ power law generalizes the time-temperature superposition principle, and suggests the validity of a TTSP, at least in the temperature and pressure ranges investigated here.

The experimental values of $\tau(T, P)$ reported in Fig. 2 provide a stringent test for the validity of the PEAG model, i.e., the Adam-Gibbs formula incorporating the effects of the pressure. The original AG model [26] gives an expression for the relaxation time as a function of the configurational entropy S_c :

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

where C_{AG} is a constant, $\Delta \mu$ is the free energy barrier (per molecule per cooperative rearranging region) to rearrangements, τ_0 is the relaxation time at very high temperatures, and S_c is defined as the excess entropy of the melt with respect to the crystal.

The excess entropy depends on both temperature and pressure and can be written as [19]

$$S_c(T, P) = S_c^{isob} + S_c^{isoth} = \int_{T_K}^T \frac{\Delta C_p(T')}{T'} dT' - \int_0^P \Delta \left(\frac{\partial V}{\partial T} \right)_{P'} dP'. \quad (3)$$

The isobaric contribution to the configurational entropy S_c^{isob} has been represented by the simple relation $S_\infty(1 - T_K/T)$, where the Kauzmann temperature T_K is the temperature at which S_c vanishes [27,28].

The isothermal contribution, S_c^{isoth} , accounts for the reduction of configurational entropy occurring when compressing the system and $\Delta(\partial V/\partial T)_{P'}$ is the difference between the molar thermal expansivity in the melt and in the crystal, respectively. This contribution to the excess entropy has been independently obtained from pressure-volume-temperature measurements performed on salol in the 0–200 MPa pressure range, at several temperatures. Experimental details are reported in Ref. [29].

Finally, the substitution of Eq. (3) into Eq. (2) gives the pressure extended Vogel-Fulcher-Tamman (VFT) expression for the relaxation time,

$$\tau(T, P) = \tau_0 \exp\left(\frac{DT_0^*}{T - T_0^*}\right), \quad (4)$$

where $D = C_{AG} \Delta \mu / S_{\infty} T_K$ is the fragility parameter at ambient pressure and the Vogel temperature is generalized accounting for the pressure effect,

$$T_0^* = \frac{T_0}{1 + S_c^{isoth} / S_{\infty}}, \quad (5)$$

where the Vogel temperature at 0 (\approx ambient) pressure takes the place of the Kauzmann temperature $T_0 \sim T_K$.

We have used D , T_0 , τ_0 , and S_{∞} , as free parameters in fitting Eq. (4) to experimental data in the bidimensional surface $\tau(T, P)$. The result of the fit is reported in Fig. 2 as solid lines showing an excellent agreement with the data in the whole T - P range. As a further support to the validity of the PEAG model, we note that it is possible to superpose the experimental values of $\tau(T, P)$ onto a single master curve as a function of the reduced temperature $(T/T_0^* - 1)^{-1}$, as shown in the inset of Fig. 2.

The values obtained for $D = 24.1 \pm 5.9$, $T_0 = 154.2 \pm 8.2$ K, and $\log_{10}(\tau_0[s]) = -22.1 \pm 1.8$ are consistent with those independently calculated from photon correlation measurements performed at ambient pressure ($D = 23.6 \pm 4.4$, $T_0 = 152.2 \pm 6.2$ K, and $\log_{10}(\tau_0[s]) = -21.1 \pm 1.4$) [30]. The value obtained for $S_{\infty} = 137.4 \pm 0.8$ J K⁻¹ mol⁻¹ is well-consistent with the one evaluated from calorimetric measurements, $S_{\infty} = 138.4 \pm 0.8$ J K⁻¹ mol⁻¹ [28]. Moreover, a comparison of the value of the Vogel temperature T_0 , obtained in this work, with those estimated for the Kauzmann temperature T_K by different techniques, (157 ± 12 K) [31,32], (167 K) [27,33], and (175.2 ± 4.2 K) [28], provides a satisfactory agreement within the error. On the other hand, some mismatch between the Kauzmann temperature T_K derived from calorimetric data and the Vogel temperature T_0 obtained from the relaxation $[\tau(T)]$ data can be expected mainly due to the approximated functions used to perform the two extrapolations, $S_c(T)$ toward 0 and τ toward ∞ [27,28]. Moreover, a further uncertainty in the determination of T_K derives from the method used to infer the configurational entropy starting from heat capacity data [28,34].

It is important to point out that the PEAG model here tested, besides to suitably describe the trend of $\tau(T, P)$ on salol, gives a rationale of the T and P phenomenology of supercooled systems. In particular, the following are observed:

(i) Experimental observations on different systems [6,8,19,35] showed a parabolic pressure behavior of the divergence temperature. It is easy to demonstrate that, in the limit of narrow T - P ranges and small variations of T_0 , the generalized Vogel temperature T_0^* , obtained from Eq. (5), can be approximated by

$$T_0^* = T_0 + bP - cP^2, \quad (6)$$

where b and c are related to the thermodynamic parameters entering into the expression of S_c^{isoth} [29].

(ii) In a recent work [11], a phenomenological VFT-like equation of state has been proposed to describe both temperature and pressure dependence of the α -relaxation time. It is now possible to derive this behavior by using the PEAG equation. Indeed, neglecting the quadratic term in Eq. (6) and taking a linear dependence of T_0^* versus P , as obtained in the 0–150 MPa pressure range investigated in Ref. [11], the Eq. (4) gives

$$\tau(T_m, P) = \tau_0' \exp\left(\frac{D_p P_0}{P_0 - P}\right), \quad (7)$$

with $\tau_0' = \tau_0 \exp(-D)$, $P_0 = (T_m - T_0)/b$, and $D_p = DT_m / (T_m - T_0) = DT_m / bP_0$. Here, τ_0 , D , and T_0 are the values of the VFT at ambient pressure, T_m is the measurement temperature, P_0 is the pressure of the ideal glass transition at a constant temperature, and b is the same reported in (i).

(iii) Paluch and co-workers [11] have also investigated the pressure dependence of fragility in an epoxy resin. They found that no pressure effect is visible in the behavior of the strength parameter D_p . This can be explained in the frame of the PEAG model recalling that $D_p = DT_m / bP_0$, which is constant in the case of a linear dependence of P_0 versus T_m observed in Ref. [11], b and D also being constant.

In conclusion, we performed photon correlation spectroscopy measurements on salol by varying both temperature and pressure. The most significant findings of this work are: (i) A TTPS is obeyed for the α -relaxation function, generalizing the time-temperature superposition with the $\omega^{-1/2}$ high-frequency α behavior recently outlined in Ref. [20]; (ii) the PEAG model, here tested on photon correlation data, suitably draws the $\tau(T, P)$ behavior in the whole T - P range. Our investigation represents a persuasive check for the PEAG model since (a) the parameters that control the temperature behavior of τ coincide, within the error, with those previously obtained in the same system by light scattering and calorimetric studies at ambient pressure; (b) the parameters responsible for the pressure dependence of τ have been independently obtained via thermodynamic measurements. These results suggest that configurational entropy plays a key role in the slow dynamics of glass forming systems. This is, in the same direction, indicated by the energy landscape approach to the glass transition highlighted by recent simulation studies (see, for example, Refs. [12–18]). The validity of the time-temperature-pressure superposition principle calls for a description of deeply supercooled (supercompressed) systems in terms of topological properties of the energy landscape. This is an important challenge for future numerical and theoretical investigations.

The authors thank A. Best [Max-Planck Institute for Polymer Research (MPIP), Mainz] for his help in the experimental collection of P - V - T measurements. S. Corezzi and S. Capaccioli are also acknowledged for many helpful discussions.

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