Slow dynamics of salol: A pressure- and temperature-dependent light scattering study

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We study the slow dynamics of salol by varying both temperature and pressure using photon correlation spectroscopy and pressure-volume-temperature measurements, and compare the behavior of the structural relaxation time with equations derived within the Adam-Gibbs entropy theory and the Cohen-Grest free volume theory. We find that pressure-dependent data are crucial to assess the validity of these model equations. Our analysis supports the entropy-based equation, and estimates the configurational entropy of salol at ambient pressure ~70% of the excess entropy. Finally, we investigate the evolution of the shape of the structural relaxation process, and find that a time-temperature-pressure superposition principle holds over the range investigated.

I. INTRODUCTION

The study of the supercooled liquid and glassy states in molecular systems is, nowadays, one of the most important topics in the physics of disordered materials. Though the molecular processes underlying glass formation still constitute an unsettled subject, some traces of universality in the behavior of highly viscous liquids near vitrification have been noticed. As general characteristics, on approaching the glass transition the structural (α) relaxation process shows (i) a non-Debye behavior of the relaxation function, and (ii) a dramatic increase of the relaxation time τ.

Different physical routes can be covered to get vitrification. Decreasing the temperature T is the common way to form a glass. However, varying the pressure P also represents an effective means. Indeed, the effects on molecular motions of an isothermal compression resemble those which are caused by an isobaric cooling. For practical reasons, cooling is generally preferred, since high pressures (of the order of MPa) are necessary to produce dynamical changes similar to those obtained by changing the temperature within few tens of degrees. Anyway, the study of the α relaxation pressure dependence can give an insight into the nature of the liquid-glass transition.

The past few years have actually seen a growing use of hydrostatic pressure in experimental investigations of glass formers (see for instance, Refs. [1–9]). Such experiments provide a more stringent testing ground for the numerous models proposed of the structural relaxation time evolution near vitrification. Among these, two are the most widely used, which are based on the free volume and configurational entropy concepts. Free volume approaches consider the decrease of unoccupied volume as the basic mechanism leading to structural arrest of a liquid system. The alternative view is that the progressive slowdown of molecular motions responsible for the glass transition is due to a reduction of the system's configurational entropy.

In this paper, we test on salol the ability of free volume and configurational entropy models to interpret the tempera-ture and pressure dependence of the structural relaxation time. Salol is a good candidate since much of the thermodynamic data are known, allowing refinement on testing theoretical models. It has intensively been studied at ambient pressure with several spectroscopic techniques, like Brillouin scattering [10], depolarized light scattering [11–13], impulsive stimulated light scattering [14], optical Kerr effect spectroscopy [15], neutron scattering [16], x-ray diffraction [17], and dielectric spectroscopy [18]. On the other hand, few experiments have been carried out by varying both temperature and pressure, namely dielectric spectroscopy [19], depolarized Raman scattering [20], and viscosity measurements [21]. Recently, some of us presented a preliminary investigation [22] on salol performed in the T and P domain by using photon correlation spectroscopy. Here, we extend our analysis through pressure-volume-temperature (*PVT*) data taken in both the supercooled and crystalline phases. We show how an appropriate use of the *PVT* results provides a realistic estimate of the configurational contribution to the excess entropy of salol. Finally, we compare our $\tau(T,P)$ data with the prediction of the pressure-extended Cohen-Grest model [23], derived in the frame of the free volume theory.

II. THEORY

A. Pressure extended Adam-Gibbs (PEAG) model

The entropy model by Adam and Gibbs (AG) [24] is based on the concept of configurational entropy and the assumption of cooperatively rearranging regions. Starting from the observation that the sluggish relaxation behavior governing the glass transition is a manifestation of a dearth of configurations accessible to the system, the AG theory states a relationship between the structural relaxation time τ and the configurational entropy S_c:

$$\tau = \tau_0 \exp\left(\frac{C_{AG}}{TS_c}\right), \qquad (1)$$

where C_{AG} is nearly constant, and τ_0 is the relaxation time at very high temperature. S_c measures the entropic contribution

arising from the possibility of a system to rearrange its structure in different configurations, which is typical of a liquid. Theoretically, a quantitative evaluation of S_c can be done in terms of the difference between the entropy of the liquid phase and the entropy of an ideal amorphous-solid phase (ideal glass) in which only vibrations (harmonic and anharmonic) and secondary relaxation processes are active [25,26]. This quantity can, in principle, be determined by computer simulations, but is inaccessible to experiments in a direct manner. Some efforts have been made to bypass a direct experimental determination of configurational entropy in a number of liquids. Unfortunately, the procedures proposed require an independent estimate of vibrational contributions to the entropy over a broad range of temperatures [27,28] or an estimate of the excess vibrational entropy at T_g [29], all of which imply nontrivial approximations. We also remark that all the previous estimates of S_c are based on temperature-dependent data alone, and are not constrained by pressure-dependent data.

Furthermore, much literature documented the extensive use of the experimentally accessible liquid over crystal (or glass) excess entropy S_{exc} in place of S_c, showing that the AG expression works well in a number of systems with S_c replaced by S_{exc} [30,31]. In this context, understanding the relationship between S_{exc} and S_c is a challenging issue. A proportionality of these two quantities at atmospheric pressure has recently been proposed [32], but a verification of such hypothesis through a relaxation experiment performed as a function of temperature alone cannot be conclusive, as the proportionality constant would simply renormalize the value of C_{AG} in Eq. (1).

Building on this background, a method based on a pressure extended Adam-Gibbs (PEAG) equation has recently been proposed by some of us [33] to analyze temperature- and pressure-dependent relaxation measurements. The pressure dependence of S_c has been introduced in Eq. (1) writing the configurational entropy of a system at a given T and P as a sum of (i) an isobaric contribution at zero pressure, $S_c^{isob}(T,0)$, and (ii) an isothermal contribution at temperature T, $S_c^{isoth}(T,P)$:

$$S_c(T,P) = S_c^{isob}(T,0) + S_c^{isoth}(T,P). \qquad (2)$$

(i) Here, the isobaric configurational term, at zero pressure, is assumed proportional to the excess entropy:

$$S_c^{isob}(T,0) = \Phi S_{exc}^{isob}(T,0). \qquad (3)$$

The parameter Φ (≤ 1) quantifies the fraction of excess entropy at $P=0$ arising from structural configurations. In addition, the excess entropy contains any contribution from secondary relaxation processes and vibrational motions [25,26,34]. It can be evaluated from the heat capacity of the liquid and the crystal, through the equation

$$S_{exc}^{isob}(T,0) = S^{liquid}(T) - S^{crystal}(T)$$
$$= \Delta S_f - \int_T^{T_f} (C_p^{liquid} - C_p^{crystal})/T' \, dT', \qquad (4)$$

where $\Delta S_f = \Delta H_f / T_f$ is the entropy of fusion.

(ii) According to the Maxwell relationship $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, the isothermal term in Eq. (2) can be written

$$S_c^{isoth}(T,P) = - \int_0^P [\Delta(\partial V/\partial T)_P] dP', \qquad (5)$$

where $\Delta(\partial V/\partial T)_P = (\partial V/\partial T)_P^{liquid} - (\partial V/\partial T)_P^{nonstruct}$ is the configurational thermal expansion at temperature T [35]. This term can be evaluated from PVT measurements as follows. The Tait equation [36] is used to describe the volume of the liquid phase as a function of T and P,

$$V^{liquid}(T,P) = V^{liquid}(T,0)[1 - C \ln(1 + P/B)], \qquad (6)$$

where C is a dimensionless constant, and $B(T)$ is well described by $B(T) = b_1 \exp(-b_2 T)$, where b_1 has the dimension of pressure and b_2 of inverse of temperature [37]. Moreover, it is reasonable to presume that the pressure dependence of the thermal expansion of the ideal glass would be much smaller than that of the liquid, and can be neglected. Accordingly, the nonstructural thermal expansion at P can be replaced by its value at $P=0$, i.e., $(\partial V/\partial T)_P^{nonstruct} \approx (\partial V/\partial T)_0^{nonstruct}$. Under these assumptions, calculating the integral in Eq. (5) yields

$$S_c^{isoth}(T,P) \approx -\left(\frac{\partial V}{\partial T}\right)_0^{liquid} \left[P + hCP - BC\left(h + \frac{P}{B}\right) \right.$$
$$\left. \times \ln\left(1 + \frac{P}{B}\right) \right] + P\left(\frac{\partial V}{\partial T}\right)_0^{nonstruct} \qquad (7)$$

where $h = 1 - b_2/\alpha$, and $\alpha = 1/V(\partial V/\partial T)_0$ is the thermal expansion coefficient at zero pressure.

In conclusion, combining Eqs. (1)–(3) provides a formula for the structural relaxation time as a function of temperature and pressure:

$$\tau(T,P) = \tau_0 \exp\left[\frac{C_{AG}}{T(\Phi S_{exc}^{isob} + S_c^{isoth})} \right], \qquad (8)$$

with S_{exc}^{isob} and S_c^{isoth} given by Eqs. (4) and (7), respectively. It is important to emphasize that the expression of S_c^{isoth}, Eq. (7), prevents the parameter Φ in Eq. (8) from playing the role of a simple renormalization constant.

B. Pressure extended Cohen-Grest (CG) model

Within a free volume picture, Cohen and Grest [23] derived a model to describe the behavior of dense liquids and glasses on the basis of a percolative approach. The existence is assumed of glasslike and liquidlike domains. The fraction p of these latter increases with temperature, and a percolative (infinite) cluster does exist above a critical concentration p_c, at which the transition from the glass to the liquid state occurs. The model predicts an analytical expression for the free volume v_f which is valid in a broad range of temperatures:

$$v_f = \frac{k}{2\xi_0} \{ T - T_0 + [(T - T_0)^2 + 4v_a\xi_0 T/k]^{1/2} \}, \qquad (9)$$

where T_0, ξ_0, and v_a are constants with the dimension of temperature, pressure, and volume, respectively. For p near

and greater than p_c, a link is established between v_f and the diffusion coefficient D, which recovers the Doolittle equation [38], $D=D_0 p\, \exp(-v_m/v_f)$, in the case of $v_m/v_f \ll \bar{\nu}$. Here, v_m is the molecular volume, D_0 is a constant, and $\bar{\nu}$ is the average size of the liquidlike clusters. A similar result is assumed for the rotational correlation time, $\tau = \tau_0 \exp(v_m/v_f)$ [39], where τ_0 is the value of τ in the limit of very high temperature under isobaric conditions. On this basis, a simple equation for the structural relaxation time in the supercooled state can be written

$$\log_{10}\tau(T) = A_{CG} + \frac{B_{CG}}{T - T_0 + [(T - T_0)^2 + C_{CG}T]^{1/2}} \quad (10)$$

where A_{CG} is related to the pre-exponential factor τ_0, and the parameters $B_{CG} = 2\xi_0 v_m \ln e/k$ and $C_{CG} = 4 v_a \xi_0 T/k$ have the dimension of temperature, and must assume positive values to have a physical meaning.

Cohen and Grest incorporate the effect of pressure in their theory by including an additional term, proportional to pressure, into their expression for the local free energy. As a consequence, the pressure dependence of the relaxation time can be obtained by changing $\xi_0 \to \xi_0 + P$. The temperature parameter T_0 is also affected by this change, via the relationship $kT_0 = kT_1 + v_a\xi_0$, with T_1 a constant, which yields $T_0(P) = T_0 + (v_a/k)P$. The final expression for $\tau(T,P)$ is

$$\log_{10}\tau(T,P) = A_{CG} + \frac{B_{CG}D_{CG}}{T - T_0^* + [(T - T_0^*)^2 + C_{CG}D_{CG}T]^{1/2}}$$

$$(11)$$

with $D_{CG} = 1 + P/\xi_0$ and $T_0^* = T_0 - (C/4\xi_0)P$. Note that this expression contains five parameters, i.e., A_{CG}, B_{CG}, T_0, C_{CG}, and ξ_0, only the first four appearing in the temperature-dependent expression at $P=0$, i.e., in Eq. (10).

III. EXPERIMENT

A. PVT measurements

Measurements of specific volume change $\Delta V(T,P)$ of crystalline and liquid salol were taken in an isothermal mode of operation by using a confining fluid technique [40]. The *PVT* data were acquired on a GNOMIX apparatus [41] described in Refs. [40] and [42]. The sample (salol) and the confining fluid (mercury) were contained in a rigid sample cell. A thin nickel foil sample cup surrounding the sample was used to guarantee hydrostatic pressure during the experiment. Silicon oil was used as pressurizing fluid. The temperature was recorded (for operational reasons) close to the sample, but actually in the pressurizing silicon oil. At a fixed temperature, starting from the low-temperature end, pressure was increased to 200 MPa, and data were recorded in pressure intervals of 10 MPa. On completion of measurements along one isotherm, the temperature setting was increased 5 K higher, and the pressure measurements were repeated. $\Delta V(T,P)$ measurements were converted into specific volume $V(T,P)$ data by using a reference density value, $\rho = 1.1742$ g cm^{-3} at $T=323.15$ K. The whole set of *PVT* measurements between $T=290$ and 380 K over the
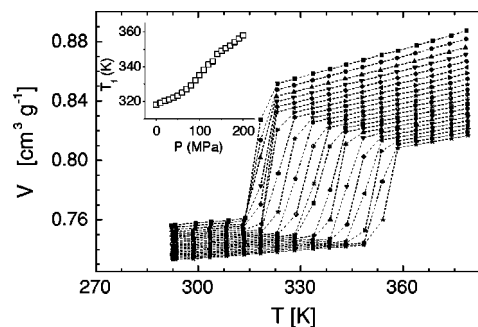

FIG. 1. Temperature dependence of the volume of salol in the crystal and liquid state at different pressures. The pressures are, from top to bottom, from 0.1 to 200 MPa in steps of 10 MPa. In the inset the melting temperature versus pressure deduced from the *PVT* measurements here reported.

0.1–200-MPa range of pressure is reported in Fig. 1. The step in the data at a given pressure marks the fusion/crystallization temperature.

B. Photon correlation measurements

Photon correlation spectroscopy (PCS) measurements under high hydrostatic pressure, up to 190 MPa, were taken at different temperatures (namely 267.1, 268.6, 271.0, 274.6, 278.3, and 280.4 K). Depolarized (*VH*) light scattering spectra were collected in the 90° geometry using an apparatus consisting of an Ar-ion laser, operating at 514.5 nm, a home made thermostated high pressure cell (a detailed description of the cell is reported in Ref. [43]), and an ALV5000E digital correlator. The scattered light was collected by a single mode fiber optics and detected by an avalanche diode (Sandercock). High pressure was generated by using nitrogen pressurized by a Nova Swiss membrane compressor and introducing the gas over steel capillaries connected with the high pressure cell. The pressure was measured by a Heise gauge with a resolution of 0.3 MPa, and the temperature by a thermocouple with a typical error of 0.1 K. Special care was taken to prepare the sample avoiding crystallization on both lowering the temperature and increasing the pressure. A cleaning procedure to have dust-free cells was used consisting of rinsing the cells with freshly distilled hot acetone. Salol [2-hydroxy benzoic acid phenyl ester, 2-(HO) $C_6H_4CO_2C_6H_5$] purchased from Aldrich company, purity 99%, was filtered (0.22-μm Millipore filter) into the dust-free cylindrical cell of 10 mm o.d. at about 80 °C. The sample was then brought back to room temperature at a very slow cooling rate. The measurements were performed following isothermal curves by varying the pressure. Each isothermal run was usually done from the higher to the lower value of pressure, this procedure assuring a shorter equilibration time before starting the measurement. Finally, we checked that the diffusion time of N_2 was long enough to prevent contamination of the scattering volume during the experiment. To this end the forward beam was continuously monitored on a black screen to directly visualize possible vertical gradients of the refractive index of the sample.
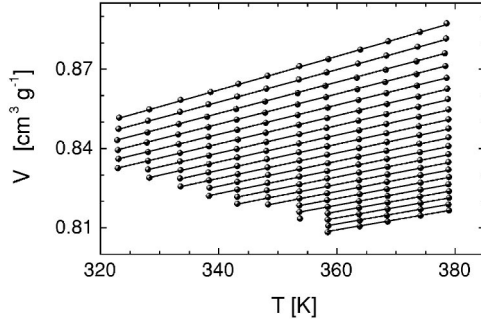
FIG. 2. Temperature dependence of the volume of salol in the liquid state. The solid lines through symbols are the best fit with the Tait equation of state, Eq. (6), with $V^{liquid}(T,0) = V_0 \exp(\alpha T)$ and $B(T) = b_1 \exp(-b_2 T)$.

IV. RESULTS

A. Thermodynamic parameters

The T and P dependence of the volume can be expressed through the Tait equation, Eq. (6), found to be valid for a wide range of materials including liquids and polymers, for changes of the volume up to 40% of the initial value. From the analysis of the data at atmospheric pressure in the liquid state we numerically find a constant value of the thermal expansion coefficient $\alpha = (\partial V/\partial T)_0^{liquid}/V^{liquid}(T,0)$, consistent with the expression $V^{liquid}(T,0) = V_0 \exp(\alpha T)$ describing the temperature behavior of the volume of liquid salol at $P = 0$ [44]. The whole set of PVT data in the liquid state is then fitted by Eq. (6). In Fig. 2 the experimental data are shown together with the result of the fit (solid lines). An excellent agreement between experimental points and fit curves is obtained with the values of the parameters V_0, α, b_1, b_2, and C reported in Table I. It is possible to recognize some generality of the parameters of the Tait equation [37]. Indeed, the values of C (~ 0.09) and b_2 ($\sim 4 \times 10^{-3}$ K^{-1}) have been found to be almost the same for a lot of materials, liquids and polymers, including chlorinated biphenyl (PCB62) [5], diglycidylether of bisphenol A (DGEBA) [6], bis-phenol-C-dimethylether (BCDE) and bis-kresol-C-dimethylether (BKDE) [7], phenylphthalein-dimethylether (PDE) [8] and cresolphthalein-dimethylether (KDE) [9]. In the crystalline phase, PVT measurements allow us to evaluate the thermal expansivity at different pressures. In particular, we find that $(\partial V/\partial T)_P^{crystal}$ ranges from about 4.5×10^{-8} m^3 mol^{-1} K^{-1} at $P = 0.1$ MPa to about 3.5×10^{-8} m^3 mol^{-1} K^{-1} at $P = 200$ MPa, with an average value $(\partial V/\partial T)_P^{crystal} \sim (4.0 \pm 0.5) \times 10^{-8}$ m^3 mol^{-1} K^{-1} over the pressure range investigated.

TABLE I. Thermodynamic parameters from the analysis of volumetric measurements.

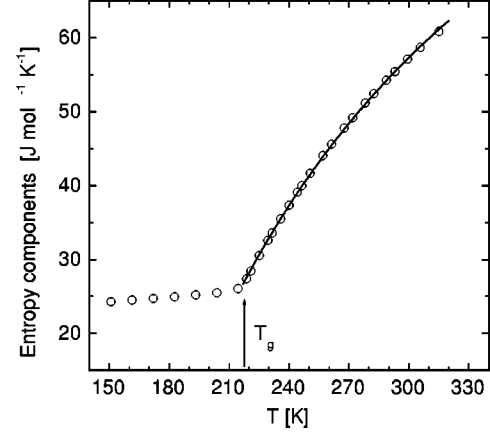|	
V_0 (m^3 mol^{-1})	$(143.8 \pm 0.1) \times 10^{-6}$
α (K^{-1})	$(7.36 \pm 0.02) \times 10^{-4}$
b_1 (MPa)	790 ± 20
b_2 (K^{-1})	$(4.70 \pm 0.06) \times 10^{-3}$
C	$(8.68 \pm 0.05) \times 10^{-2}$

FIG. 3. Temperature dependence of the excess entropy over crystal, $S_{exc} = S^{melt} - S^{crystal}$, calculated from the calorimetric data. The solid line represents the fit of the experimental data according to $S_\infty - k/T$.

The heat capacity C_p of crystalline, glassy, supercooled, and stable liquid salol at atmospheric pressure was measured by adiabatic calorimetry [45,46]. From these data, the glass transition temperature $T_g = 217 \pm 1$ K and the temperature of fusion $T_f = 315.0$ K are determined, and the excess entropy of the liquid over the crystal, $S_{exc}(T)$, is calculated by using Eq. (4), with the value $\Delta S_f = \Delta H_f/T_f = 60.83 \pm 0.04$ J mol^{-1} K^{-1} for the entropy of fusion. In Fig. 3 the experimental excess entropy is shown with circles.

B. Dynamic parameters

In the PCS experiment the homodyne technique is used, which measures the normalized time correlation function of the scattering intensity $g^{(2)}(t) = \langle I(t)I(0) \rangle / \langle I^2 \rangle$. For a Gaussian process, the intensity autocorrelation function $g^{(2)}(t)$ is related to the autocorrelation function of the scattered field, $g^{(1)}(t) = \langle E(t)E(0) \rangle / \langle |E(0)^2| \rangle$, through the Siegert equation [47]:

$$g^{(2)}(t) = 1 + f|g^{(1)}(t)|^2, \qquad (12)$$

where f is a constant. The relaxation function of a glass-forming system is generally broader than a single exponential, and experimental data are typically represented by the phenomenological Kohlrausch-Williams-Watts (KWW) function [48]:

$$g^{(1)}(t) = g_0 \exp[-(t/\tau_K)^{\beta_K}]. \qquad (13)$$

Therefore PCS spectra are fitted by using Eqs. (12) and (13). The results show an excellent agreement between experimental data and fit curves. Typical normalized homodyne correlation spectra $|g^{(1)}(t)|^2$ (symbols), taken at 267.1 K in the 88–189.5-MPa pressure range, are represented in Fig. 4 together with their KWW fits (solid lines). The values of the relaxation time τ_K and of the stretching parameter β_K have been used to calculate the average relaxation time $\langle \tau \rangle$, through the formula
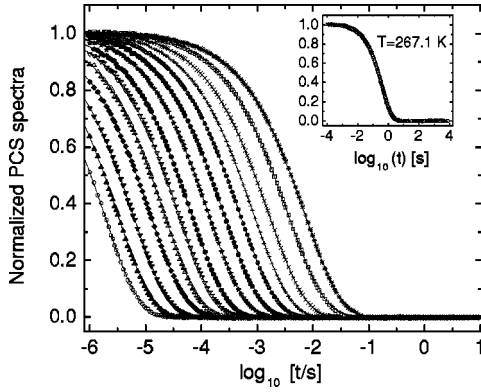
FIG. 4. Normalized photon correlation functions collected at a constant temperature of 267.1 K. Pressures from left to right are 88, 95, 102.5, 110.5, 119, 125, 132.5, 141, 148.5, 156.5, 163.5, 171, 181, and 189.5 MPa. The solid lines represent the fits to the data using the KWW function. The isothermal spectra at 267.1 K taken at different pressures rescale on a master curve as shown in the inset.

$$\langle \tau \rangle = \frac{\tau_K}{\beta_K} \Gamma \left(\frac{1}{\beta_K} \right), \qquad (14)$$

where Γ is the Euler Γ function. The values of $\langle \tau \rangle$ as a function of pressure at different temperatures are shown as symbols in Fig. 5.

Following the evolution with T and P of the shape of the relaxation function, we find that no appreciable variation is observable on the stretching parameter by changing T and P. This evidence is further supported when a master plot is drawn, showing that the spectra taken at different pressures collapse into a single curve (see inset of Fig. 4). Our determination of the stretching parameter ($\beta_K = 0.68 \pm 0.02$) agrees with previous results at ambient pressure and low tempera-
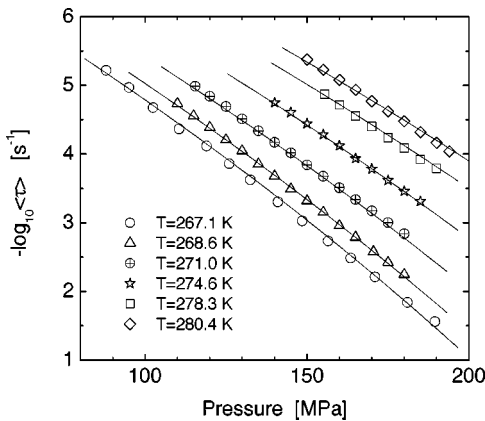

FIG. 5. Temperature and pressure-dependent structural relaxation times of salol from photon-correlation measurements. The solid lines represent the simultaneous fit with the PEAG equation [Eq. (8)] of all the experimental data, including the ones from Ref. [49] shown in Fig. 6. As explained in the text, four parameters are adjusted by the fitting procedure, in particular giving. $(\partial V/\partial T)_0^{nonstruct} = (3.8 \pm 0.7) \times 10^{-8}$ m^3 mol^{-1} K^{-1} and $\Phi = 0.68 \pm 0.08$.
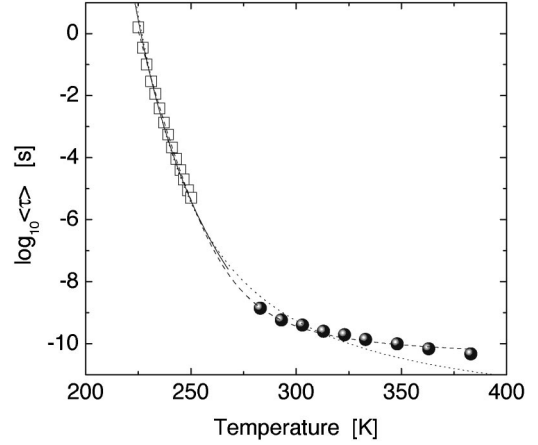

FIG. 6. Structural relaxation time of salol from depolarized light-scattering measurements at atmospheric pressure: ($\square$) depolarized photon-correlation data from Ref. [49]; (•) depolarized Brillouin and Raman light-scattering data from Ref. [11]. The solid line is the fit with the PEAG equation [Eq. (8)] through the square symbols, i.e., in the region where some cooperativity is expected. The dash line is the fit of all the data with the temperature-dependent CG equation [Eq. (10)]. The dotted line is the fit with the pressure-extended CG equation [Eq. (11)]; see also the solid lines in Fig. 7.

tures from PCS measurements: $\beta_K = 0.66 \pm 0.03$ [49], and $\beta_K = 0.60 \pm 0.08$ [50]. Different techniques, such as dielectric spectroscopy [18,49] and impulsive stimulated light scattering [51], also found a time-temperature superposition (TTS) principle to hold in salol at low temperatures. Remarkably, our results indicate the validity of a generalized time-temperature-pressure superposition (TTPS) principle in the slow dynamic regime, and support recent finding of only a modest broadening of the dielectric α peak with increasing pressure up to 0.7 GPa [19].

Moreover, Olsen *et al.* [52] recently reinvestigated TTS at low temperatures for a large number of systems concluding that a high-frequency slope of the α peak close to $-1/2$ is expected whenever TTS applies. To confront with this expectation, we first evaluate, through the relationship [53]

$$\beta_K = 0.970 \beta_{CD} + 0.144, \quad 0.2 \lesssim \beta_{CD} \lesssim 0.6, \qquad (15)$$

the value of a Cole-Davidson shape parameter, β_{CD}, corresponding to our value of β_K in the time domain. We find $\beta_{CD} = (0.55 \pm 0.02)$, and then the α peak actually decays approximately as $\omega^{-1/2}$ at high frequencies, at any temperature and any pressure considered here.

V. DISCUSSION

A. Check of the PEAG model

Our relaxation data (Fig. 5) are well in the range in which strong intermolecular cooperativity is expected for salol [18,31,54]. They can be used, together with temperature-dependent relaxation times at atmospheric pressure available in the literature [49] and reported in Fig. 6 with square symbols, to check the consistency of the PEAG model. To this

TABLE II. Thermodynamic parameters in Eq. (7) calculated from *PVT* measurements.

T (K)	P (MPa)	$|h|$	$(\partial V/\partial T)_0^{liquid}$ (m^3 mol^{-1} K^{-1})	B (MPa)
267.1	88.0–189.5	3.588	1.287×10^{-7}	225.1
268.6	110.0–180.0	3.588	1.289×10^{-7}	223.5
271.0	115.5–185.0	3.588	1.291×10^{-7}	220.9
274.6	140.0–185.0	3.588	1.294×10^{-7}	217.3
278.3	155.5–190.0	3.588	1.298×10^{-7}	213.6
280.4	150.0–194.0	3.588	1.30×10^{-7}	211.5

purpose, following Sec. II A we need to determine both the isobaric contribution at zero pressure and the isothermal contribution at temperature T of the configurational entropy, Eq. (2). The former contribution is related to the excess entropy of the liquid over its crystalline phase at ambient pressure, Eq. (3). The latter is given by Eq. (7).

The temperature behavior of the excess entropy is well described, over the whole range between T_g and T_f, by the function $S_{exc}=S_\infty-k/T$, as observed in a number of other glass formers [31]. The best fit curve corresponds to the parameters $S_\infty=137.5\pm0.3$ J mol^{-1} K^{-1}, $k=(24.05\pm0.08)\times10^3$ J mol^{-1} (see Fig. 3). Hence Eq. (3) becomes $S_c^{isob}(T,0)=\Phi(S_\infty-k/T)$, where S_∞ and k are known, and Φ will be free in the global fit with Eq. (8).

For what concerns the isothermal term, Eq. (7), the expressions $(\partial V/\partial T)_0^{liquid}=\alpha V^{liquid}(T,0)$, $h=1-b_2/\alpha$, and $B=b_1\exp(-b_2T)$ are known from the analysis of *PVT* data. Numerical details are reported in Table II. The only parameter which could not be determined experimentally is the thermal expansivity $(\partial V/\partial T)_0^{nonstruct}$ associated with nonstructural contributions. Although the value of this parameter will be derived from the fit, we expect that such a value should compare well with that measured in the crystal of salol.

Summarizing, in the fit of relaxation time data with Eq. (8) only four parameters, specifically τ_0, C_{AG}, Φ, and $(\partial V/\partial T)_0^{nonstruct}$, remain to be adjusted. The fit is carried out simultaneously in the T-P domains, over the pressure range 0.1–194 MPa at six different temperatures ($T=267.1$, 268.6, 271.0, 274.6, 278.3, and 280.4 K). The best fit curves (solid lines in Figs. 5 and 6) correspond to the values: $\log_{10}\tau_0[s]=-17.4\pm0.1$, $C_{AG}=(1.9\pm0.3)\times10^5$ J mol^{-1}, $\Phi=0.68\pm0.08$, $(\partial V/\partial T)_0^{nonstruct}=(3.8\pm0.7)\times10^{-8}$ m^3 mol^{-1} K^{-1}.

It is important to remark that the value obtained for the nonstructural thermal expansion compares well with the value calculated for the polycrystal of salol, while it is only in feasible agreement with that estimated by some of us, $(\partial V/\partial T)_0^{nonstruct}=(1.09\pm0.04)\times10^{-8}$ m^3 mol^{-1} K^{-1}, in a previous determination using a preset $\Phi=1$ in Eq. (8), i.e., obtained by replacing the configurational entropy with the excess entropy [22]. Moreover, we note that the best fit yields a value for $(\partial V/\partial T)_0^{nonstruct}$ whose uncertainty spans the variation with T and P of the crystal thermal expansion. Thus it emerges that the approximation $(\partial V/\partial T)_P^{nonstruct}\approx(\partial V/\partial T)_0^{nonstruct}$ is justified, and it is unnecessary to consider a T and P dependence of the nonstructural expansion in Eq. (5).

B. Check of the CG model

Various models interpreting the dynamics of supercooled liquids provide an equation to represent τ data as a function of temperature. Among these, the most frequently used is the Vogel-Fulcher-Tamman (VFT) equation [55]. However, its adaptability to experimental data has been demonstrated only over a limited range of temperatures. In fact, Stickel *et al.* [18,56] have shown that two VFT equations are needed to describe the relaxation data at ambient pressure for temperatures ranging from just above the glass transition up to very high temperatures, because of a change of dynamics occuring in the vicinity of a crossover temperature $T_B\approx1.2T_g$. On the other hand, the CG expression at ambient pressure, by virtue of four characteristic parameters, one more than the VFT, succeeds in describing structural relaxation times in a broad range of temperatures. Positive tests have been reported on several glass forming systems [23,57,58]. Recently, Paluch *et al.* [59] have also shown that the characteristic temperature T_0 of the CG model can be identified with T_B in a number of liquids, suggesting that the change of dynamics may be related to an onset of percolation of the free volume. However, estimates of the free volume available per liquidlike molecule founded on such a description clash with estimates extracted from dilatometric measurements [59].

An interesting and not frequently exploited testing ground for this model is the comparison with relaxation data obtained by varying both temperature and pressure. To do this, in the case of salol, we analyze the available temperature-dependent relaxation times at atmospheric pressure [11,49], using Eq. (10), and compare the results with those obtained with the addition of our data at variable pressure, using Eq. (11).

Depolarized light-scattering measurements on salol performed at atmospheric pressure by photon-correlation spectroscopy [49] and Brillouin and Raman spectroscopy [11] are reported in Fig. 6, spanning a wide time-temperature range. The fit parameters of Eq. (10) are: $A_{CG}=(10.6\pm0.1)$, $B_{CG}=(91\pm13)$K, $C_{CG}=(3.4\pm0.4)$K, and $T_0=(265\pm3)$K, confirming that T_0 matches the crossover temperature $T_B\sim265$ K [56,59].

Then, with the addition of our $\tau(T,P)$ data, we test the generalized CG equation. In case all of the five parameters in Eq. (11) are left adjustable the fitting algorithm gives a number of solutions. We note that the sign of C_{CG} controls the concavity of the curves as a function of P, with the solutions with $C_{CG}>0$ (physically acceptable) having an upward concavity and the solutions with $C_{CG}<0$ (albeit physically unacceptable) having the correct downward concavity. A similar result has also been obtained for an epoxy system [60]. We find only one solution with $C_{CG}>0$, corresponding to the set of parameters $A_{CG}=12.6$, $B_{CG}=580$ K, $T_0=220$ K, $C_{CG}=6.4$ K, and $\xi_0=160$ MPa. The inability of the CG equation to represent the variation of τ with both temperature and pressure is apparent in Figs. 6 and 7, where, respectively, the dotted line and the solid lines are generated by Eq. (11) with the best fit solution above. The first four of these parameters differ significantly from those which describe the ambient pressure data alone, indicating that even a fair description at
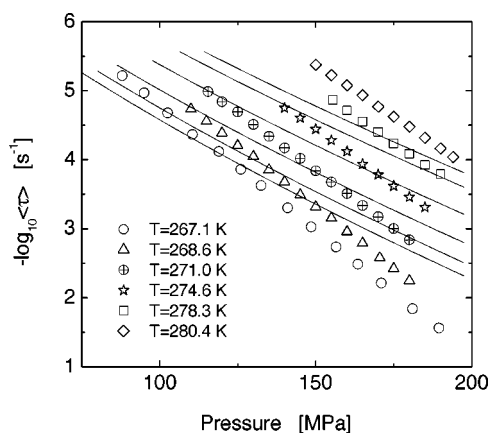
FIG. 7. Temperature- and pressure-dependent structural relaxation times of salol from depolarized light-scattering measurements. The solid lines represent the simultaneous fit with the pressure-extended CG equation [Eq. (11)] of all the experimental data, including the ones at atmospheric pressure from Refs. [49] and [11] shown in Fig. 6; see text for details.

ambient pressure is lost. Notably, when the fit is performed fixing A_{CG} (or T_0) to the value obtained from the fit of the data at ambient pressure, the bad fit of the high pressure data remains qualitatively unchanged, while a good description of the data at $P=0.1$ MPa is recovered (curves not shown in Figs. 6 and 7 for clarity) with all the free parameters within the error of those obtained from Eq. (10).

The inapplicability of the generalized CG equation prompts disfavor towards the robustness of the CG theory. Nevertheless, the free volume approach remains physically attractive, and we cannot exclude that the inadequacy of Eq. (11) to describe the $\tau(T,P)$ data might be ascribed to the number of simplifications used to derive the equation, which are possibly no longer valid at high pressures.

VI. CONCLUSIONS

In conclusion, we have studied the slow dynamics of salol under variable temperature and pressure using PCS in combination with *PVT* measurements. Comparing the behavior of the structural relaxation time with equations derived within the AG entropy theory and the CG free volume theory, we find that pressure-dependent data are crucial to assess the validity of model equations of the glass transition. In particular, we confirm previous work [60] showing that the pressure-dependent expression of τ predicted by the CG model cannot reproduce the experimental data, despite the presence of five adjustable parameters and an ability to parametrize $\tau(T)$ data over a broad temperature range at ambient pressure. Instead, experimental $\tau(T,P)$ data conform to the entropy-based PEAG equation. Interestingly, since the parameters which control the pressure dependence of τ have separately been determined via *PVT* measurements, this equation requires only four adjustable parameters in the T and P intervals investigated in the present work. Remarkably, the deduced parameters yield physical results. Especially, the fraction of excess entropy which arises from structural configurations is realistically estimated (~70% at ambient pressure).

In an effort to determine the role played by volume and thermal effects in driving molecular dynamics, Casalini *et al.* [19] have recognized that neither temperature nor volume is the dominant variable governing the structural relaxation of salol near T_g, consistently with results for a number of other glass formers [7,61]. Conceptually, this result accords with our findings that the dominant thermodynamic variable is configurational entropy, a quantity which embodies both temperature and volume effects: different relative contributions to τ of thermal energy and volume reflect a different sensitivity of the number of explored configurations to changes of temperature and volume. We believe that the positive test of the PEAG model presented here should stimulate further work on other glass formers and by different techniques.

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