Correlation between nonexponential relaxation and non-Arrhenius behavior under conditions of high compression

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Photon correlation spectroscopy was used to investigate the behavior of the dynamical properties of 1,1'-di(4-methoxy-5-methyl-phenyl)cyclohexane (BMMPC) at elevated pressures. The fragility of BMMPC measured by the steepness index m_T is decreasing and the nonexponentiality parameter β_{KWW} is increasing with increasing pressure. This result strongly suggests that the phenomenological correlation between the steepness index and nonexponentionality is also preserved under high compression. The pressure dependence of the structural relaxation times is well characterized by a simple activation volume form. The activation volume continuously increases with decreasing temperature, which is probably due to the increase of cooperativity of the structural relaxation process. Moreover, we found that the glass-transition temperature exhibits a significant dependence on pressure.

I. INTRODUCTION

An important aspect of the liquid-glass transition is the effect of temperature on the structural (α-) relaxation time of a liquid near glass transition. It has been suggested by Angell that on the basis of the temperature dependence of the structural relaxation time in the vicinity of the glass-transition temperature one can simply identify the structure stability of glass formers with regard to a temperature change [1–3]. According to the above idea fragile liquids are structurally less stable because the temperature dependence of their relaxation time is much stronger than the usual Arrhenius behavior. On the other hand, strong liquids exhibit almost Arrhenius behavior and, thus, more stable structure. The fragility parameter (or steepness index) is usually quantified from the slope of the Arrhenius plot at the glass-transition temperature [4],

$$m_T = \frac{\partial \log \tau}{\partial (T_g/T)}\bigg|_{T=T_g}. \tag{1}$$

As temperature dependence of the relaxation time is often analyzed in terms of the Vogel-Fulcher-Tammann (VFT) law [5]: $\tau = \tau_0 \exp[B/(T-T_0)] = \tau_0 \exp[D_T T_0(T-T_0)]$, the steepness index can be also calculated using the VFT parameters [6]

$$m_T = \frac{1}{\ln 10} \frac{B T_g}{(T_g - T_0)^2}. \tag{2}$$

The question whether different patterns of temperature dependence of the relaxation time in any way reflect local

structure of the glass-forming liquid near glass transition and are correlated to other liquid properties is still vitally debated [4,7–15]. On the basis of theoretical considerations, Vilgis [16] pointed out, among other things, that the fragility parameter can be mapped onto the fluctuation of the coordination number, Δz. As a consequence glass formers with $\Delta z = 0$ (network glasses) are always strong systems whereas materials with $\Delta z > 0$ turn out to be fragile.

In the framework of the coupling model, the idea of "fragility" takes a completely different sense [11,12,17,18]. This model relates the degree of the cooperativity of local dynamics with the shape of the relaxation function. On the other hand it is established that the steepness index correlates with the degree of deviation from the exponential relaxation [4] (Debye behavior) which is usually measured by means of the stretching exponent in the Kohlrausch-Williams-Watts function. Thus, the behavior of the temperature dependence of the structural relaxation time also reflects the role, played by many-body interactions (cooperativity).

It is generally believed that fragility is an important material constant since many correlations between the fragility parameter and a number of other liquid properties have been demonstrated [4,11–15]. Probably the most spectacular and widespread correlation, as mentioned above, is that between the steepness index and the nonexponentiallity (non-Debye relaxation) [4]. Unfortunately, some exceptions from the above correlation were also reported recently [4,19]. The dielectric measurements in propylene carbonate, cresolphthalein-dimethylether (KDE), and phenolphthalein-dimethylether (PDE) have shown that only on the basis of the temperature dependencies of the dielectric relaxation time these materials can be characterized as fragile liquids. On the other hand, analyzing the shape of the dielectric relaxation (DR) function one can classify them as strong materials due to a large value of the nonexponentiality parameter (stretching exponent). In a recent high-pressure study we have shown [20] that for PDE this discrepancy is not observed in the dynamic light scattering (DLS) data: The non-

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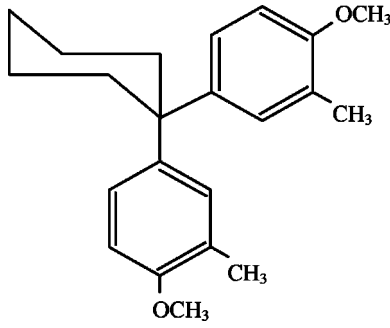†Also at Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany.

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FIG. 1. The structural formula of BMMPC.

FIG. 2. Isobaric temperature dependencies of the structural relaxation time at labeled pressures. The solid lines represent fits using the VFT law.

exponentiality parameter obtained from DLS is lower than that obtained from the DR measurements as expected for a fragile glass-forming liquid. Different shapes of the dielectric and light scattering correlation functions might result from different coupling of the probes (dipole moment and optical anisotropy, respectively) to the dynamics of the entire molecule and have been discussed in [20].

In the last decade there has been growing interest in the effect of compression on the dynamics of glass-forming liquids close to the glass transition [21–39]. It is well known that the pressure variation brings about the changes in molecular packing of a liquid and thus influences intermolecular interactions. Since the glass-transition temperature usually strongly depends on compression, therefore, temperature dependence of the structural relaxation time is also a function of pressure. However, it is not clear whether pressure also alters fragility and the degree of molecular cooperativity. In particular one can put forward an important question whether the correlation between fragility and nonexponentiality is still valid under the condition of high compression.

In this paper we examine the dynamics of a low molecular weight glass-forming liquid: 1,1'-di(4-methoxy-5-methyl-phenyl)cyclohexane (BMMPC) over wide temperature and pressure ranges. The structural relaxation times are probed using the dynamic light scattering technique. We found that the steepness index (fragility) is correlated with the nonexponential behavior of the relaxation function also under the conditions of high compression.

II. EXPERIMENT

The experimental setup for high-pressure depolarized dynamic light scattering-photon correlation spectroscopy measurements and the experimental procedures were described elsewhere [21]. This experimental setup consists of an Argon-ion laser, a high-pressure light scattering cell, an avalanche diode detector and ALV5000 digital correlator. The sample was pressurized using nitrogen (1–2000 bar).

BMMPC was synthesized in the laboratory of Professor H. Sillescu at the Johannes Gutenberg University, Mainz, Germany. The chemical structure of BMMPC is shown in Fig. 1.

III. RESULTS AND DISCUSSION

The time correlation functions $g^{(1)}(t)$ measured in a photon correlation experiment were analyzed using the empirical
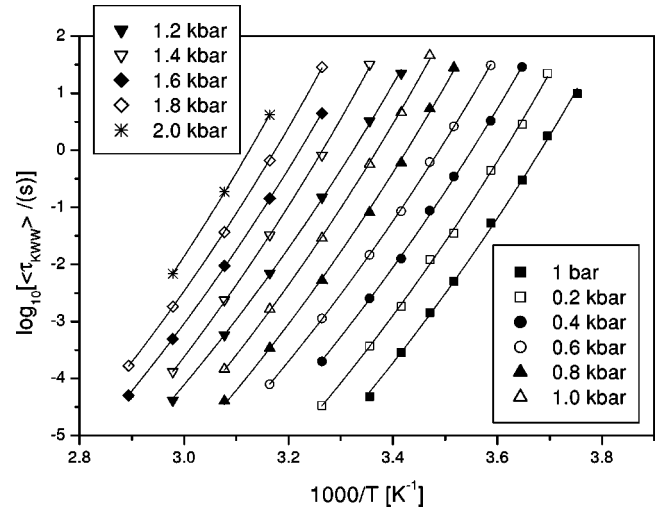
Kohlraush-Williams-Watts formula [40],

$$g^{(1)}(t) = A \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{\beta_{KWW}}\right]. \quad (3)$$

From the analysis we obtained the values of the structural relaxation time τ_{KWW} and the nonexponentiality parameter β_{KWW} at various temperatures and pressures. The behavior of the structural relaxation time is most commonly discussed in terms of the average KWW relaxation time $\langle \tau_{KWW} \rangle$, defined as

$$\langle \tau_{KWW} \rangle = \frac{\tau_{KWW}}{\beta_{KWW}} \Gamma(\beta_{KWW}^{-1}), \quad (4)$$

where $\Gamma(\beta_{KWW}^{-1})$ is the Gamma function.

To determine the behavior of fragility under high compression a standard procedure was applied. As a measure of fragility we have chosen the steepness index defined by Eq. 2. The temperature dependence of the average structural relaxation time in our temperature range is well described by the Vogel-Fulcher-Tammann law. In Fig. 2 we present the isobaric relaxation times plotted versus inverse temperature. It is evident that an increase of pressure is accompanied by a substantial shift of the isobars towards higher temperatures. Thus, one can expect that the glass-transition temperature strongly depends on pressure. A detailed discussion concerning the pressure dependence of T_g will be given later in this paper. Very recently, on the basis of the Adam-Gibbs model [41], Casalini and coworkers [42] pointed out that the combined pressure and temperature dependence of the structural relaxation time in glass formers can be well described by means of the VFT law with a constant (pressure independent) value of the strength parameter D_T and pressure dependent T_0. Thus, we reanalyzed the isobaric data from Fig. 2 using the VFT law and assuming that D_T is now a common fit parameter for all analyzed isobars. Again a good agreement of the experimental data and the fits was achieved for D_T
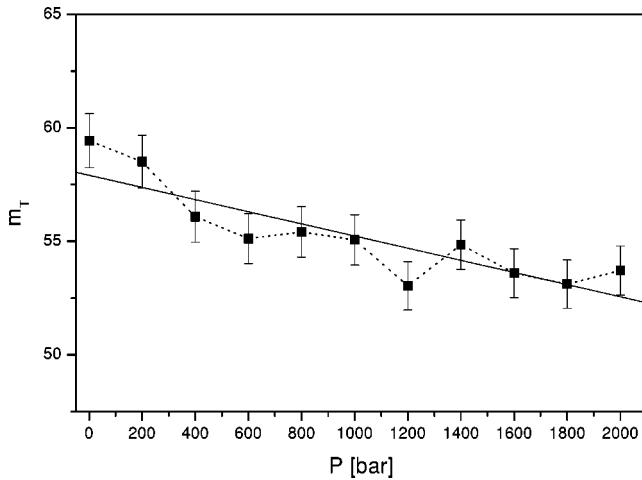
FIG. 3. The pressure behavior of the steepness index (fragility) determined from the VFT fits with a common D_T parameter and Eq. (2) for all analyzed isobars. The solid line represents a linear fit to the data.

$=27.5\pm2$. It should be mentioned that on the basis of the dielectric relaxation measurements Stickel *et al.* [43] showed also a good agreement of the data with the VFT law for $t >10^{-6}$ s. Moreover, Meier *et al.* [44] found that the relaxation times measured by both experimental methods have nearly the same values at a given temperature. We also observed a coincidence of our data with the dielectric relaxation times measured by Stickel [45].

According to Eq. (2), the values of the fragility parameter at a given pressure were calculated using the fit parameters of the VFT law. In order to eliminate errors related to extrapolation we have chosen T_g as the temperature at which the relaxation time is equal to 10 s. The behavior of the steepness index determined at different pressures is displayed in Fig. 3. These results show that the fragility of BMMPC is decreasing with pressure. Note that thanks to the assumption D_T=const the error bars of m_T are relatively small.

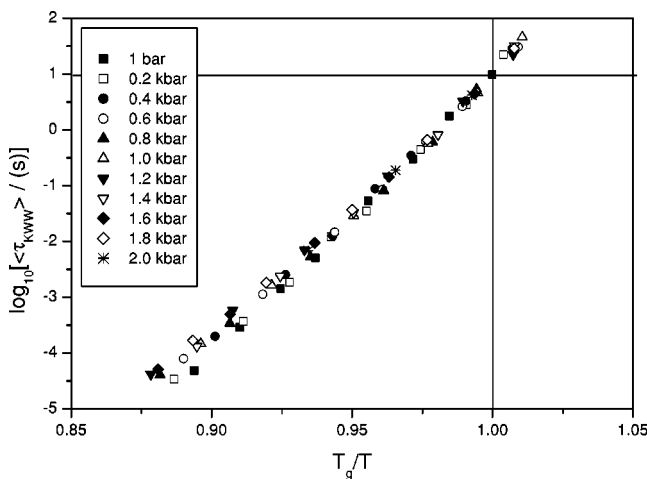To corroborate this result we also plotted in Fig. 4 the

FIG. 4. The influence of compression on the fragility is demonstrated by means of T_g-scaled Arrhenius plots.
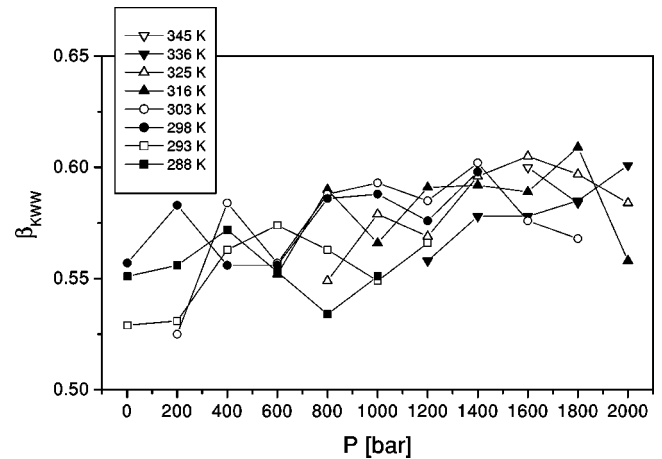

FIG. 5. The stretching parameter β_{KWW} determined from the isothermal data versus pressure.

isobaric relaxation data versus reduced temperature: T_g/T. If fragility were pressure independent all the data should collapse onto a single master plot. It is evident from Fig. 4 that the fragility parameter m_T is slightly decreasing with pressure. It is noteworthy that a very similar behavior of the steepness index, i.e., a small decrease of m_T with compression in the low-pressure range was also observed in some epoxy glass-forming liquids [21,22].

Taking into account the correlation established between nonexponential relaxation and fragility [4] it is of interest to examine the behavior of the β_{KWW} parameter at elevated pressure. The effect of pressure on nonexponentiality (measured by the value of β_{KWW}) is shown in Fig. 5. Despite a substantial experimental error one can see that the β_{KWW} value is slightly increasing in the entire pressure range by about 0.02. In order to relate this change to a corresponding change of the fragility m_T we can use the phenomenological relationship [4],

$$m_T=250(\pm30)-320\beta_{KWW}. \qquad (5)$$

Thus, the estimated change of the fragility parameter m_T due to the pressure effects is given by: $\Delta m_T(P)= -320\Delta\beta_{KWW}(P)$. Taking $\Delta\beta_{KWW}(P)=0.02$ for our pressure range of 1–2000 bar (Fig. 5) we obtain $\Delta m_T(2000$ bar$)=-6.4$ in a good agreement with our data in Fig. 3. This result provides a strong indication that the correlation between m_T and β_{KWW} holds also under high-pressure conditions. An alternative explanation of our findings is offered by the model developed by Vilgis [16]. The decrease of the value of m_T with pressure suggests a narrowing of the distribution of the coordination number (decrease of Δz). This might suggest that the local order is increasing upon compression. However, to support this idea structural studies have to be carried out at elevated pressures.

As structural relaxation times were measured with the same temperature steps we can easily plot isothermal dependencies. The behavior of $\log_{10}\langle\tau_{KWW}\rangle$ as a function of pressure is shown in Fig. 6. It is seen that all presented data exhibit nearly linear dependence indicating that at least in
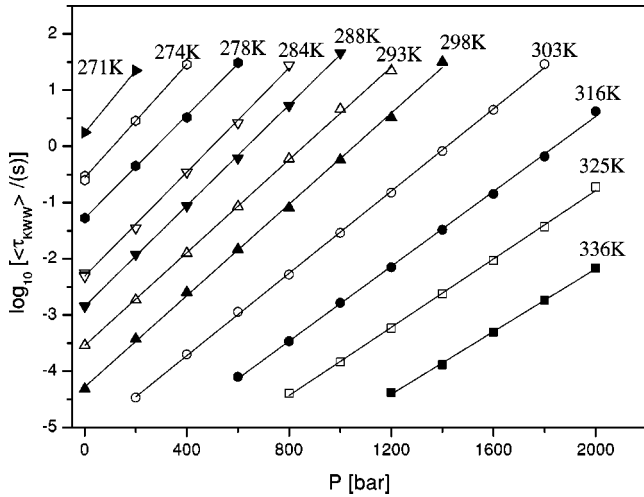
FIG. 6. The isothermal pressure dependencies of the structural relaxation time at given temperatures. The data are fitted by means of a simple activation volume formula (solid lines).

this pressure range the relaxation time can be well described by means of a simple activation form

$$\tau = \tau_0 \exp\left(\frac{P \Delta V^{\#}}{RT}\right), \qquad (6)$$

where $\Delta V^{\#}$ denotes the activation volume and R is the gas constant. An analogous pattern of behavior is often observed in low molecular weight glass-forming liquids with nearly spherical shape of the molecules. As an example one can mention KDE, PDE, ortho terphenyl (OTP) [19,20,46]. From the analysis carried out for the data in Fig. 6 we determined the values of the activation volume. The results for $\Delta V^{\#}$ are presented in Fig. 7. The plot shows that the activation volume increases as temperature decreases. The data collected in the literature imply that such behavior is observed in many other materials and can be considered as a specific feature of the dynamics of supercooled liquids and amorphous polymers. Since the activation volume reflects the volume re-
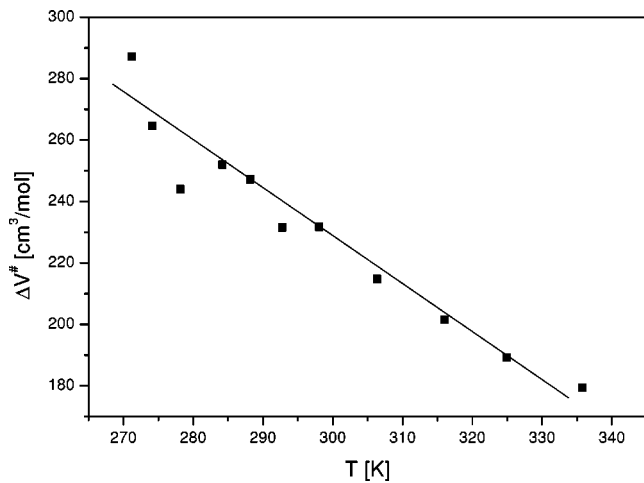

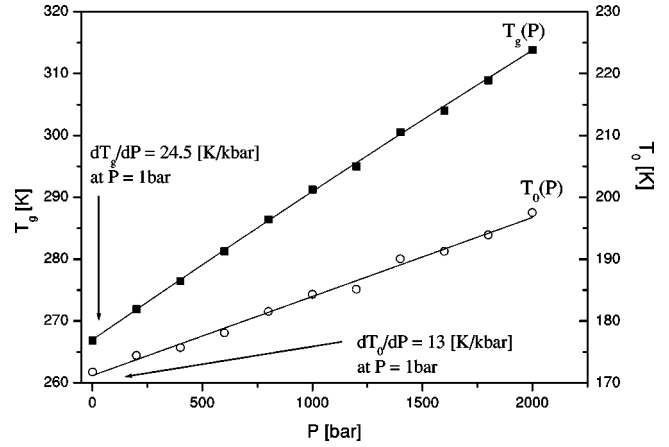FIG. 7. Activation volume versus temperature. The straight line is a guide for the eye.

FIG. 8. Pressure dependence of the glass-transition temperature and T_0. The second-order polynomial was fitted to $T_g(P)$ data whereas pressure dependence of T_0 can be well parameterized by a linear function.

quirements for relaxation, therefore its increase with lowering temperature is attributed to an increase in the cooperativity of the relaxation process.

Finally, we also examined the effect of pressure on the glass-transition temperature. Herein we identify T_g as a temperature at which $\langle \tau_{KWW} \rangle = 10$ s. This results in $T_g = 267$ K (at atmospheric pressure). If we extrapolate our data to $\langle \tau_{KWW} \rangle = 100$ s, as conventionally used to define the glass-transition temperature, we obtain $T_g(100 \text{ s}) = 262$ K in a good agreement with the literature value of 261 K [44] measured by means of the differential scanning calorimetry. The values of T_g determined from the isobaric dependencies of the relaxation times are displayed in Fig. 8. The glass-transition temperature of BMMPC is strongly dependent on pressure. To parameterize this data we employed a quadratic function. Consequently, the value of the slope at ambient pressure, was found to be equal to 25 K/kbar. It should be noted that the behavior of the glass-transition line, i.e., the curvature and slope are very close to that observed for other low molecular weight glass-forming liquids with similar molecular shape and interactions, such as OTP, KDE, PDE. Thus, the pressure dependence of the glass-transition temperature reflects the molecular crowding generated by compression as well as the nature of the intermolecular interactions. In Fig. 8 we also plotted the pressure dependence of T_0 which can be well parameterized by means of a linear function. It is noteworthy that the value of the slope at ambient pressure determined for the $T_0(P)$ line is much smaller than for $T_g(P)$ dependence. General dependence between T_g, T_0, their pressure derivatives and fragility will be discussed in a separate paper [47].

IV. SUMMARY AND CONCLUSIONS

Photon correlation spectroscopy was used to investigate the behavior of the dynamical properties of BMMPC at elevated pressures. The results of our analysis show that the fragility of BMMPC measured by the steepness index m_T is decreasing with increasing pressure. Also the nonexponenti-

ality parameter β_{KWW} behaves in a consistent way, i.e., it is increasing with increasing pressure. The changes of both parameters m_T and β_{KWW} fulfill the phenomenological scaling [4]. This result strongly suggests that the correlation between the steepness index and nonexponentiality is also preserved under high compression.

It was shown that pressure dependence of the structural relaxation time is well characterized by a simple activation volume form. We found that the activation volume continuously increases with decreasing temperature. This behavior is probably due to the increase of cooperativity of the structural relaxation process. Moreover, we found that the glass-transition temperature exhibits a significant dependence on pressure. These observations are in agreement with the results reported in the literature for other glass formers with similar molecular shape and intermolecular interactions.

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