Temperature and Pressure Scaling of the α Relaxation Process in Fragile Glass Formers: A Dynamic Light Scattering Study

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The dynamics of two fragile glass forming liquids was studied as a function of temperature and pressure using dynamic light scattering. On the basis of measured data we evaluated the pressure and temperature scaling of the α relaxation. All the isotherms can be superimposed and form a master curve when the reduced relaxation times are plotted versus reduced pressure. The Kohlrausch-Williams-Watts stretching parameter β_{KWW} is increasing with increasing temperature and decreasing pressure and plotted versus $\log\langle\tau_{\mathrm{KWW}}\rangle$ follows a master curve at all temperatures and pressures studied.

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The understanding of the structure and dynamics of supercooled liquids and the liquid-glass transition is of great importance for many disciplines from the manufacturing of inorganic and polymeric glasses of desired properties used in everyday life to biophysical problems such as protein structure and dynamics, food preservation, and suspension of life of desert insects during drought. The liquid-glass transition can be induced either by decreasing temperature or increasing pressure of the system. In most cases the glass transition is studied by measuring the temperature dependence of viscosity or relaxation time of the supercooled liquid. Only in a few cases the pressure dependence of these parameters was measured by light scattering [1–4], dielectric relaxation [5–8], viscosity [9–11], specific heat [12,13], and quasielastic neutron scattering [14]. These studies were carried out both in low molecular weight (e.g., *o*-Terphenyl, glycerol, dibutyl phthalate, isopropylbenzene) and polymers [e.g., polyisoprene, poly(propylene glycol)]. However, there is as yet no theoretical model describing both the temperature and pressure dependence of the structure and dynamics of supercooled liquids using physically meaningful parameters.

High pressure dielectric measurements have played an important role in the study of long time dynamics of supercooled liquids. On the basis of isothermal measurements, it was demonstrated that the pressure dependence of dielectric relaxation time can be described in an analogous way to the temperature dependence at ambient pressure [15,16], whereas isobaric data provided some information on the effect of pressure on fragility in several glass formers [17–19]. Recently, pressure dependence of fragility extracted from viscosity measurements has been discussed [10,11]. However, the viscosity data were mainly used to test the free volume concepts [10,11]. On the other hand, behavior of short time dynamics under conditions of high compression was studied by incoherent neutron scattering and light scattering [2,14]. The interest of the influence of pressure on fast dynamics was stimulated by the introduction of the mode-coupling theory (MCT) [20].

Glass forming liquids have been classified into two classes: strong and fragile liquids [21,22], depending on the form of the temperature dependence of their viscosity (structural relaxation time) on approaching the glass transition temperature T_g. While strong liquids follow Arrhenius temperature dependence of these parameters, the fragile liquids exhibit strongly non-Arrhenius behavior. Some strong liquids can become more fragile under high hydrostatic pressure which can be related to their polymorphism. In a review paper on glass transition [23], studies of the behavior of liquids near T_g at high pressure were listed as one of the key problems in the field. Because of the obvious experimental difficulties, not much has been done since then.

In temperature dependent studies of the glass transition both density and thermal effects are involved. In order to separate the contributions of density and thermal effects to the glass transition and to understand the role played by each of them, both pressure and temperature dependence has to be measured. The aim of this work was to describe the temperature and pressure dependence of the dynamics of supercooled liquids using a universal scaling approach and a convenient definition of the fragility.

Dynamic light scattering–photon correlation spectroscopy measurements under high hydrostatic pressure (up to 1600 bar) were performed for two fragile liquids: poly(bisphenol A-co-epichlorohydrin), glycidyl end capped (PBG), and diglycidyl ether of bisphenol-A (EPON 828) with molecular weights 374 and 190, respectively. The light scattering setup consisted of an Ar-ion laser, a high pressure cell [3], and an ALV5000E digital correlator. A monomode optical fiber and an avalanche diode (Sandercock) were used to detect the scattered light. The sample was filtered into a dust free round cell (12 mm outer diameter) and was pressurized using nitrogen. The measured autocorrelation functions were fitted using the Kohlrausch-Williams-Watts (KWW) formula:

$$g^{(1)}(\tau) = a + B\exp\left[-\left(\frac{\tau}{\tau_{\mathrm{KWW}}}\right)^{\beta_{\mathrm{KWW}}}\right]. \qquad (1)$$

The average KWW relaxation time $\langle\tau_{\mathrm{KWW}}\rangle$ is calculated from the values of τ_{KWW} and β_{KWW} obtained from the fit and is defined as

$$\langle\tau_{\mathrm{KWW}}\rangle = \frac{\tau_{\mathrm{KWW}}}{\beta_{\mathrm{KWW}}}\,\Gamma\left(\frac{1}{\beta_{\mathrm{KWW}}}\right), \qquad (2)$$

where $\Gamma(1/\beta_{\mathrm{KWW}})$ is the Gamma function.

The effect of pressure on $\langle\tau_{\mathrm{KWW}}\rangle$ in PBG is presented in Fig. 1. The evolution of the relaxation times with pressure is most commonly described using the activation form

$$\tau = \tau_A \exp\left(\frac{PV^{\#}}{RT}\right), \qquad (3)$$

where $V^{\#}$ is the activation volume. According to the above equation the relaxation time in Fig. 1 should exhibit linear dependence of $\tau(P)$ in a semilog scale. However, it was found that all isotherms show a curvature. In the superpressed state, the relaxation times increase more rapidly with increasing pressure than it results from the activation form. To describe the behavior of the light scattering average relaxation times we used a phenomenological expression introduced to characterize pressure evolution of the dielectric time constant in fragile glass-formers [7,16]:

$$\tau = \tau_a \exp\left(\frac{D_P P}{P_0 - P}\right), \qquad (4)$$

where τ_a denotes the corresponding relaxation time measured under atmospheric pressure, P_0 is the pressure of the ideal glass transition at a constant temperature, and D_P is a dimensionless parameter defined analogously to D_T in the temperature-dependent Vogel-Fulcher-Tammann (VFT) equation.

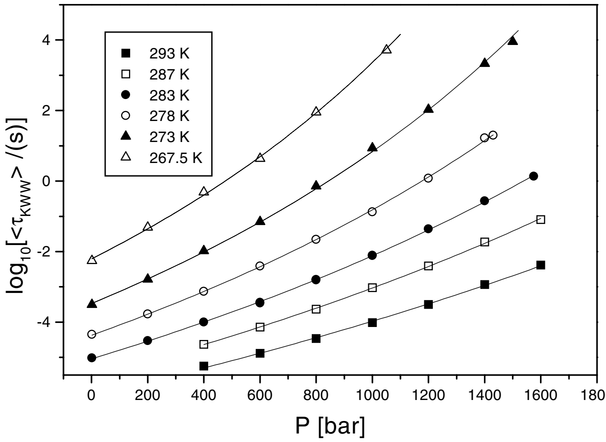

FIG. 1. Isothermal values of average relaxation time $\langle\tau_{\mathrm{KWW}}\rangle$ obtained from dynamics light scattering in PBG. The solid lines represent fits to the data using Eq. (4).

By fitting Eq. (4) to the isotherm at $T = 283$ K we obtained the value of the parameter $D_P = 33$ which was used to parametrize all other isotherms. Such an approach provides a satisfactory description of all isotherms with only one free parameter P_0. The analogous analysis was carried out for EPON 828 with a constant value of $D_P = 27.5$ for all isotherms. As a consequence, we found that the experimental values of $\tau(P)$ can be successfully superposed onto a single master curve for all measured temperatures (see Figs. 2a and 2b). This superposition is possible only when reduced relaxation time $\tilde{\tau} = \frac{\tau}{\tau_a}$ is plotted versus reduced pressure $\tilde{P} = (\frac{P_0}{P} - 1)^{-1}$.

The stretching parameter β_{KWW} obtained from the fitting procedure is plotted versus $\log[\langle\tau_{\mathrm{KWW}}\rangle]$ in insets in Figs. 2a and 2b. These results prove that: first, β_{KWW} is pressure and temperature dependent; second, changes in values of β_{KWW} are nearly the same when the dynamics is controlled by temperature or pressure changes. Very small devations of β_{KWW} from the master curve are observed

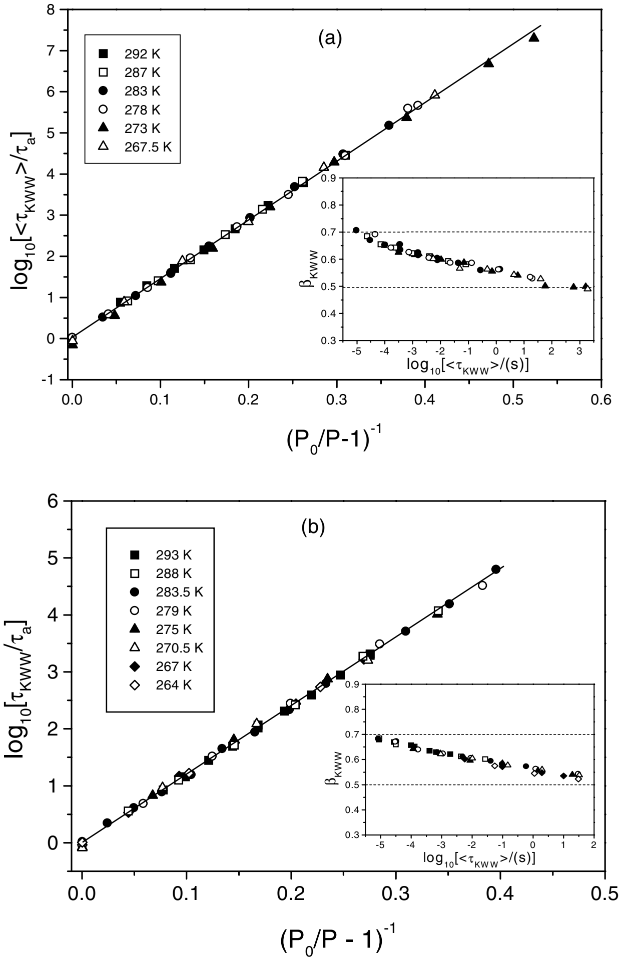

FIG. 2. The data in the main area of figures are normalized by plotting reduced relaxation time $\langle\tau_{\mathrm{KWW}}\rangle/\tau_a$ against reduced pressure $(\frac{P_0}{P} - 1)^{-1}$. Insets show stretching parameter β_{KWW} determined from isobaric and isothermal data versus $\log\langle\tau_{\mathrm{KWW}}\rangle$. (a) and (b) refer to PBG and EPON 828, respectively.

only for EPON 828. Since the value of the β_{KWW} parameter in PBG near the glass transition is the same for different pressures, one can expect that the fragility parameter D_T is pressure independent. A validation of such prediction can be checked by analysis of T_g-scaled activation plots (or "Angell plots"), in which $\log[\langle\tau_{\mathrm{KWW}}\rangle]$ is plotted versus T_g/T [21]. On the basis of such Angell plots, one can characterize liquids by the slope of the Angell plot at the glass transition temperature:

$$m(T) = \left[\frac{\partial \log\tau}{\partial T_g/T}\right]_{T_g}. \qquad (5)$$

It is easy to see in Fig. 3a that all isobars have the same slope at $T_g/T = 1$. This means that fragility defined in this way, indeed, does not change with compression. On the other hand, for EPON 828 we have found a very small change in the slope of isobars for various pressures, indicating that fragility is weakly pressure dependent. Note that the parameter β_{KWW} also exhibits the similar behavior in the vicinity of the glass transition temperature.

For the isothermal pressure dependence of the relaxation times $\tau(P)$ we can define a steepness index in analogy to Eq. (5):

$$m(P) = \left[\frac{\partial \log\tau}{\partial P/P_g}\right]_{P_g}. \qquad (6)$$

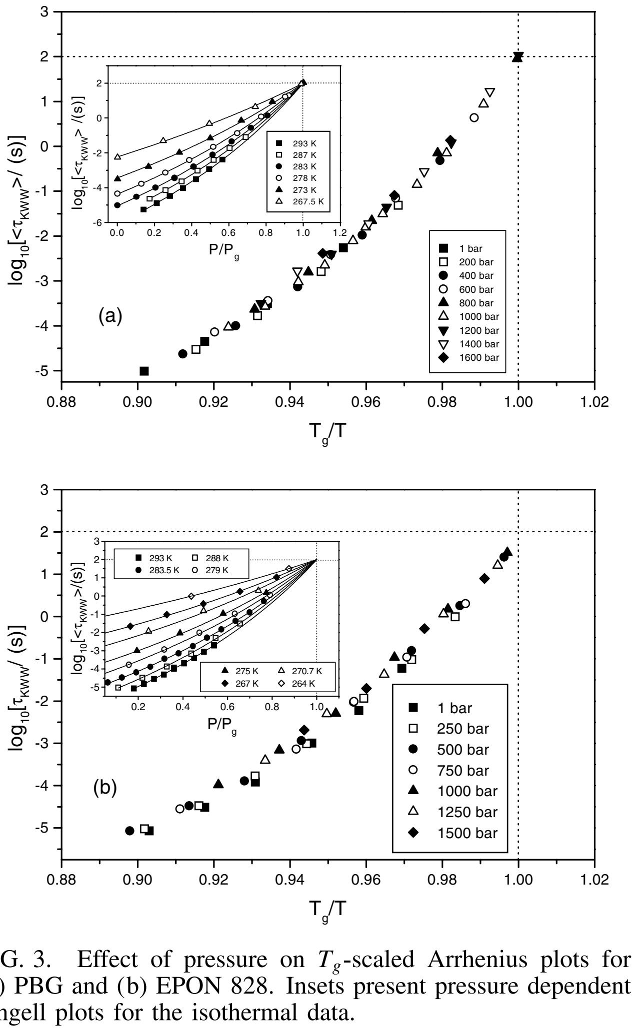

FIG. 3. Effect of pressure on T_g-scaled Arrhenius plots for (a) PBG and (b) EPON 828. Insets present pressure dependent Angell plots for the isothermal data.

Such modified Angell-plots for PBG and EPON 828 are presented in the insets in Figs. 3a and 3b, respectively. In this kind of scaling the steepness index [Eq. (6)] is not constant and depends on temperature. Thus, it cannot be used for classification of glass forming liquids in the pressure dependent studies. Therefore, we proposed to characterize liquid behavior during copression by means of the isothermal fragility parameter D_P [Eq. (4)].

In this Letter, we have reported extensive studies of density and thermal effects on the dynamics of supercooled liquids. For isothermal data, the pressure analog of the VFT law [Eq. (4)] provides a good fit and parameter D_P accounts for the isothermal fragility of glass formers. Since D_P is temperature independent, it is possible to superpose different isotherms onto a single master curve. In this context it may be interesting to note that similar scaling behavior was also found for high-pressure viscosity data of low molecular weight glass forming liquids [24].

The isobaric fragility D_T obtained from the isobaric data is almost pressure independent (only a slight decrease of fragility of EPON 828 can be observed). On the basis of our data we can also construct isothermal pressure dependent Angell plots. It is evident that relaxation times expressed in terms of the reduced variable P/P_g cannot be superimposed. Only the fragility parameters D_T and D_P obtained from the VFT law and Eq. (4), respectively, allow for an unequivocal characterization of glass-forming liquids in the temperature and pressure dependent studies.

Finally, the α relaxation is analyzed using a KWW relaxation function with a single parameter β_{KWW} characterizing nonexponentiality of the relaxation. We found that the value of β_{KWW} decreases as glass transition is approached both by decreasing temperature and increasing pressure. The scaling of nonexponentiality parameter stems from pressure independence of isobaric fragility in accordance with correlation between nonexponential relaxation and non-Arrhenius behavior [21].

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