

## Analysis of “equation of state” for supercooled liquid

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The pressure and temperature dependent dielectric relaxation times are compared with the predictions of the model proposed by Avramov. Remarkable agreement is found in whole  $P$  and  $T$  plane. It was also pointed out that the tested model predicts no pressure effect on fragility and nonlinear character of pressure dependence of glass transition temperature. Our data provide also an assessment of the generalized Vogel–Fulcher–Tammann (VFT) law. However, it is inferred that the generalized VFT law is not able to accurately reproduce the surface described by experimental relaxation times. Additionally, isothermal data are analyzed by the pressure counterpart of the temperature VFT law. The isothermal data expressed in terms of the reduced relaxation time and reduced pressure form a master curve. © 2000 American Institute of Physics.

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### INTRODUCTION

A rapid increase of the characteristic relaxation time,  $\tau$ , or viscosity,  $\eta$ , on approaching the glass transition is observed by different experimental techniques. Such behavior is a physical manifestation of the strong slowing down of molecular motions in a supercooled liquid. One of the key problems concerning this issue is to find a theoretical model describing the evolution of the relaxation time (or viscosity) in the full thermodynamical space. The great majority of both theoretical and experimental works have focused mainly on temperature effects at ambient pressure. A number of phenomenological models have been proposed for the description of temperature evolution of  $\alpha$ -relaxation process.<sup>1–10</sup> The most commonly used function for fitting  $\tau(T)$  dependence is the Vogel–Fulcher–Tammann (VFT) law:<sup>1</sup>

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right). \quad (1)$$

However, analysis of experimental data based on the method proposed by Stickel<sup>11,12</sup> revealed that the VFT law is successful in describing the data only in limited range of temperatures.<sup>13,14</sup> In fact, none of the functions proposed in the literature seem to be able to reproduce experimental results over the entire temperature range.

Alternatively to cooling, the  $\alpha$ -relaxation dynamics can be controlled by compression of a liquid. The employment of pressure as an additional thermodynamical variable affords possibilities to explore several fundamental aspects related to dynamics of glass-forming liquids, i.e.,

- (i) the pressure dependence of relaxation time,
- (ii) the effect of pressure on the fragility of a liquid,

- (iii) the effect of pressure on the glass transition temperature,  $T_g$ .

During recent years, considerable effort has been done to measure the time constant of the  $\alpha$ -relaxation process covering a broad range of time scales.<sup>15–18</sup> These measurements show that the relaxation time, or viscosity, exhibit a nonexponential pressure dependence.<sup>19–22</sup> For most glass formers the continuous increase of the  $\alpha$ -relaxation time during compression can be well parameterized by the pressure counterpart of the VFT law:<sup>18,19,23</sup>

$$\tau = \tau_0 \exp\left(\frac{D_P P}{P_0 - P}\right). \quad (2)$$

Up to now we considered separately the influence of pressure and temperature on the relaxation times. A more general approach, however, requires taking into account the combined effects of  $P$  and  $T$ . This naturally leads to searching for the “equation of state,”  $\tau(T, P)$ , for the glass-forming liquids. The knowledge of temperature and pressure dependence of the relaxation times is particularly important whenever one is interested in the behavior of liquid fragility and glass transition temperature under the condition of high compression.<sup>21,22</sup>

Very recently, a new model, which provides the analytical expression for the temperature–pressure dependence of viscosity, was proposed by Avramov.<sup>24</sup> The model is based on a hypothesis that the motion of molecules is a thermally activated process with a jump frequency

$$\nu_i(E)_i = \exp\left(\frac{E_i}{RT}\right). \quad (3)$$

By calculation of the average jump frequency for Poissonian distribution, Avramov worked out the relationship between the viscosity and entropy of a system:

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$$\eta = \eta_{\infty} \exp \left\{ \frac{E_{\max}}{\sigma_r} \exp \left[ -\frac{2(S - S_r)}{ZR} \right] \right\}. \quad (4)$$

In this equation  $E_{\max}$  denotes the maximal value of the activation energy,  $\sigma_r$  is the dispersion in the reference state with entropy  $S_r$ , and  $Z$  is the degeneracy of the system

According to the above model, the glass transition takes place when the disorder in the amorphous system decreases to the extent that dispersion of the activation energy barrier is only 3.5% of its maximal value. Then, based on the thermodynamical consideration, the following equation of state was derived:

$$\eta = \eta_{\infty} \exp \left\{ 30 \left( \frac{T_r}{T} \right)^{\alpha} \left( 1 + \frac{P}{\Pi} \right)^{\beta} \right\}, \quad (5)$$

with

$$\beta = \frac{2\kappa_0 V_m}{ZR} \Pi = \alpha \frac{\kappa_0 V_m}{C_p} \Pi,$$

where  $\kappa_0$  is the volume expansion coefficient at ambient pressure,  $C_p$  is the specific heat capacity,  $V_m$  is the molar volume, and  $\Pi$  is a constant parameter. As the viscosity is usually simply proportional to the relaxation time of the system (as, for example, measured by the dielectric response<sup>25,26</sup>) the formula obtained by Avramov could be used to analyze dielectric data.

The principal objective of our study is to test the model proposed by Avramov in the case of dielectric relaxation times measured over a wide range of pressure and temperature in poly[(phenyl glycidyl ether)-*co*-formaldehyde] (PPG). In the framework of this paper we also discuss other phenomenological approaches introduced to analysis high-pressure data.

## EXPERIMENT

The pressure and temperature dependent measurement were carried out in Poly[(phenyl glycidyl ether)-*co*-formaldehyde] (PPG) which was supplied by Aldrich Chemicals. PPG can be classified as the fragile system<sup>27</sup> with a high-pressure coefficient  $(dT_g/dP)_{P=0.1 \text{ MPa}} = 0.156 \text{ K/MPa}^{-1}$ . Due to this fact, one can expect that even moderate pressures, below 100 MPa, may possibly be sufficient to induce significant changes of relaxation times. The glass transition temperature as determined from differential scanning calorimetry is  $T_g = 264 \text{ K}$ .

Dielectric measurements were performed in the frequency range from 10 mHz up to 10 MHz by using two different measurements systems—a frequency response analyzer (Solartron SI-1260) and an impedance analyzer (HP-4192A). The capacitor consists of two parallel stainless steel plates separated by a quartz spacer and has a nominal geometric capacitance of about 10 pF. The electrode set is mounted inside the cylindrical capsule. After filling the dielectric cell with the tested liquid it is placed in a high-pressure chamber. Deformation of the Teflon membrane (the upper base of cylindrical capsule is covered by a Teflon membrane) enables the transmission of pressure changes to the tested sample which is only in contact with the stainless

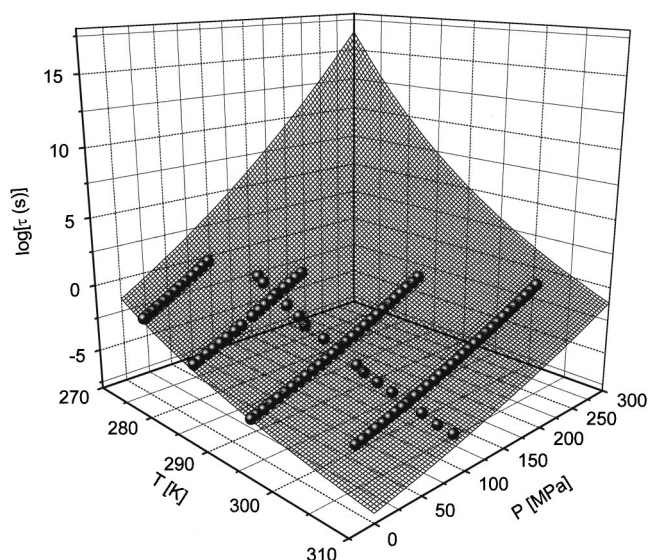


FIG. 1. Behavior of the relaxation times in  $P$ - $T$  plane. The experimental points were compared with the model proposed by Avramov, Eq. (5) (the wire surface).

steel, Teflon, and quartz. The pressure was measured by a Nowa Swiss tensometric pressure meter with a resolution of 0.1 MPa. The temperature was controlled to within 0.1 K by means of a liquid flow provided by a thermostatic bath. A more detailed description of the experimental setup with the diagram of the high-pressure dielectric cell can be found in Ref. 28.

## RESULTS AND DISCUSSION

The dielectric measurements of the frequency dependence of the complex permittivity  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$  were carried out as a function of pressure and temperature. From the imaginary part of permittivity,  $\epsilon''(\omega)$ , it is possible to determine a characteristic relaxation time for the  $\alpha$  process as the reciprocal of frequency of loss maximum, i.e.,  $\tau = (2\pi f_{\max})^{-1}$ . We observed that the  $\alpha$ -relaxation peak moved continuously toward the lower frequencies, both compressing and cooling the studied system.

Figure 1 shows how  $\tau$  varied with temperature and pressure in  $\log[\tau(s)]$ ,  $P$ ,  $T$  representation. It can be seen that the experimental data describe the two-dimensional surface. Below we used the model proposed by Avramov [Eq. (5)] in order to check the possible existence of such a surface. The wire surface in Fig. 1 represents the result of fitting Eq. (5) to the data. The equation of state parameters obtained numerically are  $\alpha=7.75$ ,  $\beta=2.23$ ,  $\Pi=465 \text{ MPa}$ ,  $T_r=257 \text{ K}$ , and  $\log[\tau_0(s)] = -10.4$ . Excellent agreement with experimental data is confirmed in Fig. 2, which shows experimental isotherms and the corresponding cross section of the fitted surface (solid lines).

A convenient way of testing the applicability of the expression proposed by Avramov is in terms of the temperature independent master function  $\phi$  formulated based on Eq. (5):

$$\phi = \beta \log \left( 1 + \frac{P}{\Pi} \right) = \log \left( \log \frac{\tau}{\tau_0} \right) - \log \left( 13 \left( \frac{T_r}{T} \right)^{\alpha} \right). \quad (6)$$

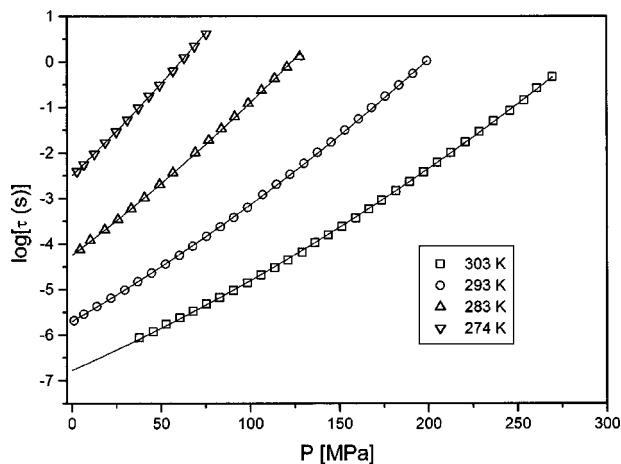


FIG. 2. Logarithm of the relaxation time versus pressure. The opened symbols and solid lines indicate the isothermal data point and corresponding cross sections of fitted surface, respectively.

By applying the above function for the abscissa in Fig. 2, it should be possible to obtain a master plot. It is evident from Fig. 3 that all isotherms can be successfully superposed onto such a master curve.

We continue our analysis based on Eq. (5) to ascertain that Avramov's model properly describes the experimental findings. To attain a reliable test, the pressure-derivative method, which reduce the number of remaining fits parameters, was employed. Stickel *et al.* previously used an analogous method to examine the details of  $\log[\tau(s)]$  data as a function of temperature for a series of glass-forming liquids.<sup>11,12</sup> Since only the relaxation times determined from the pressure measurements feature a relatively high accuracy, we restricted the analysis to the isothermal data. In the upper inset of Fig. 3 we have plotted  $\log[\tau(s)]$  vs  $(1 + (P/\Pi))^\beta$ , which reveals the linear behavior of  $\tau(P)$  dependence. Good agreement with experimental data is confirmed by its derivative behavior displayed in the bottom right-hand inset of Fig. 3.

In our recent work<sup>27</sup> we showed, based on isobaric measurements in PPG, that the fragility of this system is pressure

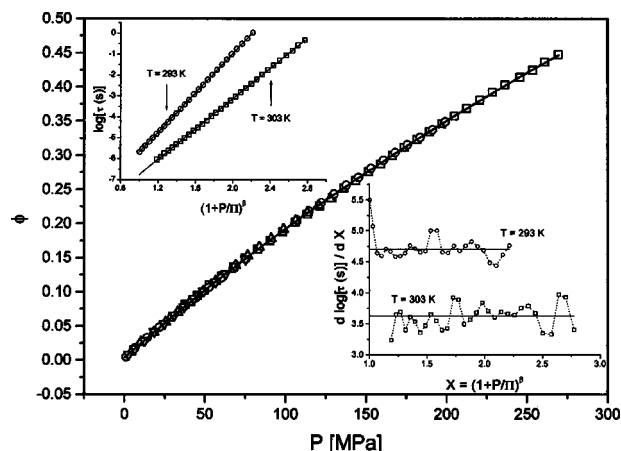


FIG. 3. The master plot for isothermal data according to Eq. (5). Two isotherms (293 K and 300 K) in linear representation are shown in the top left-hand inset. Derivative plots are depicted in the bottom right-hand inset.

independent, within the experimental error. The values of fragility in Ref. 27 were calculated using the definition of fragility for the relaxation data introduced by Angell and co-workers:<sup>29</sup>

$$m = \frac{d \log \tau}{dT/T_g} \Big|_{T=T_g} \quad (7)$$

In connection to the above we have posed the question of whether the model discussed here also predicts no pressure effect on fragility. A relationship between fragility and pressure can be easily found by combining Eqs. (5) and (7):

$$m = \alpha A \left( \frac{T_r}{T_g(P)} \right)^\alpha \left( 1 + \frac{P}{\Pi} \right)^\beta, \quad (8)$$

where  $A = 30 \log e$ .

In the above expression, the glass transition temperature is pressure dependent,  $T_g(P)$ . To find an analytical form for  $T_g(P)$  we take into account the dynamical definition of the glass transition,<sup>29</sup> according to which the glass point is identified by temperature, at which the relaxation time reaches a characteristic value, usually taken to be 100 s. Then,  $T_g(P)$  dependence can be also extracted from Eq. (5):

$$T_g(P) = T_r \left( \frac{A}{2 - \log \tau_0} \right)^{1/\alpha} \left( 1 + \frac{P}{\Pi} \right)^{\beta/\alpha}. \quad (9)$$

This equation expresses the well-established experimental fact that the pressure dependence of the glass transition temperature is generally nonlinear.<sup>30-34</sup> Thus comparing Eqs. (5) and (7), we obtained the following expression for fragility:

$$m = \alpha(2 - \log e), \quad (10)$$

which is pressure independent. The above result is in perfect agreement with our recent findings. The value of the fragility parameter,  $m$ , which was determined by Eq. (10), is equal to 96. It should be also stressed that the latter equation establishes a very important relation between the so-called dynamical fragility,  $m$ , and the thermodynamical fragility, which is defined as  $\alpha = 2C_p/ZR$ .

In the first section of presented work we mentioned that isothermal data can also be successfully described by means of the pressure counterpart of the temperature VFT law. Therefore, it is of interest to compare the fitting results obtained from both models [Eqs. (5) and (2)]. Such comparison is carried out for an isotherm measured in  $T = 293$  K and is depicted in Fig. 4. By fitting Eq. (2) to the experimental data, the following values of parameters were obtained:  $P_0 = 1040$  MPa and  $D_p = 56.4$ . On the other hand, the third parameter,  $\tau_0$ , which denotes the relaxation time at ambient pressure, was taken from experiment. Thus Eq. (2) includes only two adjustable parameters. For both models excellent agreement of fits and data can be stated. In Fig. 4 fits with Eq. (2) and Eq. (5) are shown as dotted and solid lines, respectively. It is very difficult to distinguish both curves in the whole range of pressure. Differences between these models would probably be noticeable by measuring the relaxation times of the order of few hours (see inset in Fig. 4).

In further analysis we prove that, based on Eq. (2), it is also possible to construct a master curve. To this end, all

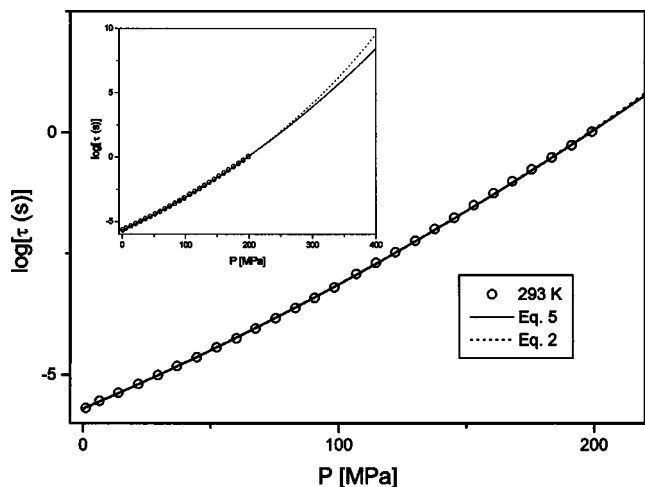


FIG. 4. The comparison fitting results obtained by Eq. (5) (solid line) and Eq. (2) (dotted line) for isotherm  $T=293$  K. Differences between both equations can be observed for very slow relaxation time (out of our measurement possibilities) as displayed in the inset.

other isotherms from Fig. 2 were parameterized using Eq. (2) with a fixed value of isothermal fragility,  $D_p=56.4$ . Such an approach provides satisfactory description of all isotherms with only one free parameter  $P_0$ . The master curve can be form when the reduced relaxation time,  $\log[\tau/\tau_0]$ , is plotted versus reduced pressure,  $((P_0/P)-1)^{-1}$ . It becomes obvious from Fig. 5 that all isotherms are successfully superposed onto one single curve. The analogous master plot was also reported for high-pressure viscosity data in low-molecular-weight glass-forming liquids. Additionally, the derivative method was used to check the linearity of these data. The behavior of derivatives, depicted in the inset of Fig. 4, indicates that Eq. (2) well reproduces  $\tau(P)$  dependence.

Finally, we also considered a generalized VFT equation, which was proposed by Fytas *et al.*<sup>35</sup> to analyze pressure and temperature dependent data obtained from photon correlation studies. The model is based on the assumption that param-

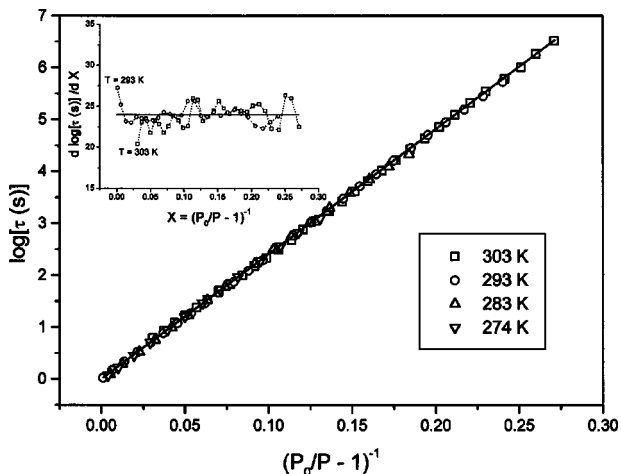


FIG. 5. The normalized data by plotting reduced viscosity against reduced pressure. A derivative method is applied to check linearity of these data (see inset).

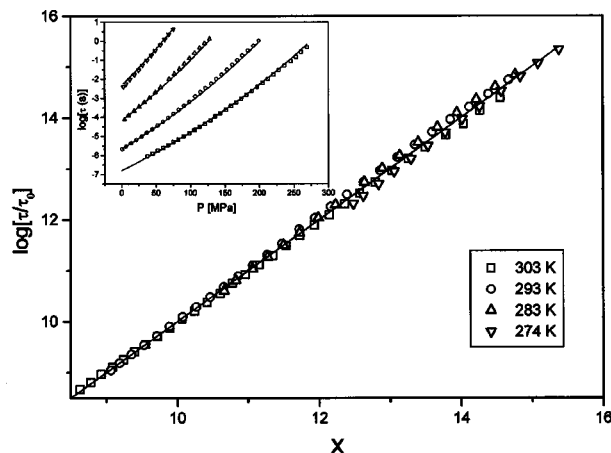


FIG. 6. Fits of isothermal data obtained from the generalized are the VFT law depicted in the inset. The main area of the figure presents the master plot:  $\log[\tau/\tau_0]$  vs  $X=(B+aP)/[T-(T_0-bP)]\log e$  (solid line). The symbols represent the experimental data.

eters  $B$  and  $T_0$  in the temperature VFT law [Eq. (1)] are linearly dependent on pressure and yield the following expression:

$$\tau = \tau_0 \exp\left(\frac{B+aP}{T-(T_0-bP)}\right). \tag{11}$$

It is also noteworthy that the extended VFT law, contrary to the model of Avramov, predicts linear  $T_g(P)$  dependence. Using the analogous fitting procedure as in the case of the Avramov model, the following values of parameters are obtained:  $a=1.93$ ,  $b=0.077$ ,  $B=1463$  K,  $T_0=223$  K,  $\log[\tau_0(s)]=-14.7$ . Unfortunately, the generalized VFT law is not able to describe the relaxation time in the whole range of  $T$  and  $P$ . Poor agreement with experimental data is demonstrated in the inset of Fig. 6. As a consequence it is not possible to superimpose all of the pressure dependent data on a master curve (see the main area of Fig. 6). The experimental points deviate significantly from the master line (solid line) in the slow relaxation time range. This result indicates that assuming the linear  $B(P)$  and  $T_0(P)$  dependencies in the VFT relation is not sufficient to adequately reproduce the surface of the relaxation times. On the other hand, it is not unlikely that such assumptions can be justified only in the case of small pressure range.<sup>35,36</sup>

We can state that both the five-parameter function of Avramov and the pressure counterpart of the VFT law provides the best description of pressure effect on the  $\alpha$ -relaxation process in PPG. However, it is difficult to come to clear conclusions which lead to a better fits. Even analysis based on the derivative method is not able to resolve these ambiguities within the studied range of pressures.

### CONCLUSIONS

We have studied the behavior of dielectric relaxation time in the  $T$ - $P$  plane. The combined effects of  $P$  and  $T$  on relaxation times are analyzed based on the model proposed by Avramov, as well as the extended VFT law. It was proven that only the Avramov approach gives good representation of our experimental data. Additionally, we pointed out that this

model predicts the pressure independent value of fragility and nonlinear character of pressure dependence of glass transition temperature, which is in good agreement with our previous experimental findings. Moreover, the important relationship between dynamical and thermodynamical fragility was established.

For isothermal data, we also obtained good fits by means of the pressure counterpart of the VFT law. Using reduced relaxation times and reduced pressure, it is possible to superimpose all isotherms on a single master plot. This result indicates that parameter  $D_p$ , which accounts for the isothermal fragility of the glass former, is temperature independent in studied system.

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