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Pressure-Induced Change in the Relaxation Dynamics of Glycerol

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Glycerol is one of the best studied and most widely used glass-forming liquids; however, its dynamic properties are still under discussion. The dielectric spectra of glycerol are studied in detail over wide ranges of temperatures and pressures up to 4.5 GPa. Starting from the pressures of 2–3 GPa, qualitative change in the dynamics of structural relaxation processes in glycerol has been revealed. It is accompanied by the appearance of secondary relaxation and a change in the asymptotic behavior of the pressure dependence of the fragility. The relation between the parameters for different relaxation mechanisms is analyzed.

As the temperature decreases or the pressure increases, many liquids important for applications do not crystallize but manifest an exponential increase in viscosity; as a result, a material acquires solid state properties while remaining in a structurally disordered noncrystalline state. Thus, it becomes rather difficult to theoretically describe the dynamic characteristics of supercooled liquids: although the first attempts toward this description were made as early as the 1920s [1–5], there is no universally adopted theoretical model that could quantitatively describe glass former behavior. In recent decades, interest in this matter has increased due to advances in experimental possibilities and new experimental data.

Panoramic dielectric spectroscopy is a convenient method for studying the dynamic characteristics of supercooled liquids. The frequency dependences of the complex permittivity of the glass formers usually have some relaxation features. The most pronounced structural relaxation (or α relaxation), which is, like viscosity, a collective effect, is characterized by the strong exponential dependence of the relaxation time on the temperature and pressure and is observed in the range of up to 15–18 frequency decades [6–8]. Moreover, most glass formers exhibit the higher-frequency secondary (β-) relaxation processes, which can be in the form of a pronounced supplementary absorption peak of a lower amplitude and, usually, of a weaker temperature dependence of the relaxation time, or can be in the form of the broadening of the absorption α peak attributed to the additional power-low contribution (the excess wing (EW)). The origin of the secondary relaxation processes are much less studied and are presently under active discussion. For example, the secondary relaxation can be attributed both to the oscillations of the molecule as a whole (the Johari–Goldstein (JG) type [9]) and to the mutual displacements of its separate parts. It is stated [10, 11] that the JG-type, non-cooperative relaxation process is a precursor of structural relaxation and, hence, should always be observed, although no general opinion exists on its genesis and spatial localization [12]. A detailed classification of the secondary relaxation processes is presented in [10–12].

Glycerol is one of the most thoroughly studied glass formers whose dielectric absorption spectra for normal pressure have no pronounced secondary peak. The precise dielectric measurements demonstrated [7] that the high-frequency flank of the α peak in the absorption spectrum includes a EW-type feature, which increases in its amplitude and is transformed to a “shoulder” when the sample is held for several weeks at a constant temperature [13–15] or is subjected to the external pressure in the subgigapascal range [16–20]. The excess wing in glycerol was assumed [13, 18, 21] to be the high-frequency slope of the secondary JG peak masked by a more intense α peak; however, the low magnitude of the effect prevented the unambiguous determination of its origin.

The measurements under pressure are very interesting for the investigation and classification of various dynamic effects in the glass formers, because various

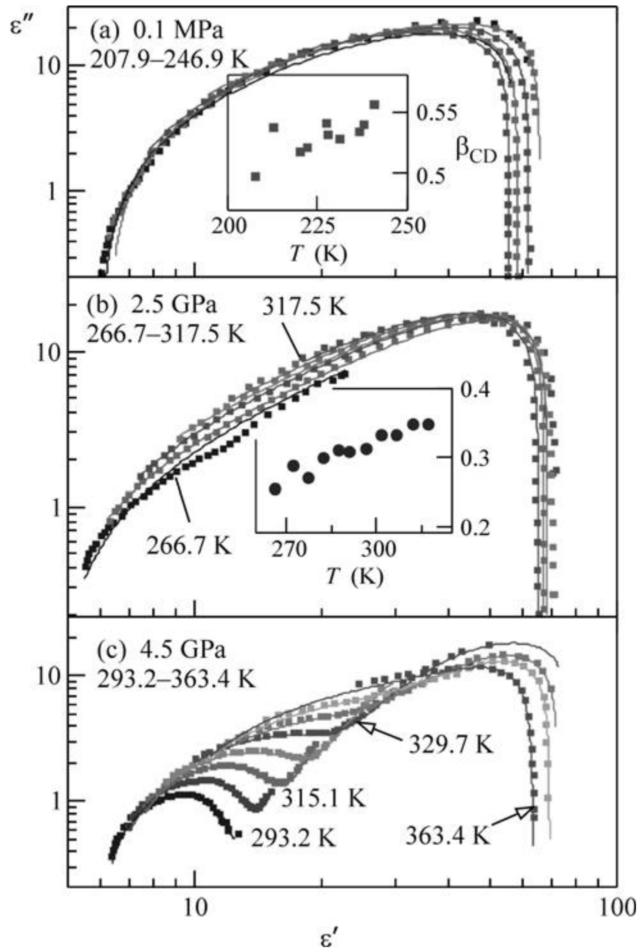

Fig. 1. Cole–Cole diagrams for the spectra of glycerol at different temperatures for (a) normal pressure, (b) the intermediate pressure range, and (c) high pressures. The points are the experimental data, the lines in panels (a) and (b) are the approximations by function (1), and the lines in panel (c) are the approximations by the sum of Eqs. (1) and (2). The insets illustrate the temperature dependences of β_{CD} in Eq. (1).

relaxation features have significantly different pressure sensitivities [10, 11, 22–24]. The use of the pressure as the control parameter appears to be particularly important in the excess wing case, because the variation of the temperature shifts the excess wing synchronously with the α peak so that these features always superpose on each other. For example, it was shown in [23] that the compression of tripropylene glycol, which features β relaxation under normal pressure, first results in the excess wing that is then transformed into the relaxation peak with a further increase in the pressure. Even more unusual behavior was revealed in m-fluoroaniline [25]: as the pressure is increased, the β peak caused by hydrogen-bond-induced clusters is suppressed, and the excess wing is transformed to a new absorption peak corresponding to the genuine JG relaxation.

The first measurements of the spectra of glycerol under pressure of up to 5 GPa were performed more than 40 years ago [20]. However, the high pressure equipment used in [20] could not provide reliable results of appropriate quality for pressures higher than 2 GPa. In the past 15 years, several attempts have been made at measuring the dielectric spectra of glycerol under pressure [16–19, 26], but the pressures in those works did not exceed 1–2 GPa. At the same time, the calculations [27, 28] predict that the dynamic characteristics of the liquid–glass transition should considerably change at the pressure above a certain threshold value (about 3 GPa for glycerol). The key objective of this work is the detailed investigation of the evolution of relaxation dynamics in glycerol under superhigh pressures. It has been found that the spectra of glycerol under pressure change qualitatively; in particular, the secondary (β) relaxation in the dielectric spectra was observed [29]. Detailed analysis of the behavior of the parameters of various spectral features with the temperature and pressure allowed us to follow the crossover between two types of the relaxation dynamics.

The experiments were carried out on an original spectrometer [29] built around a toroid-type, high-pressure cell [30], where the overall deformation of the container with the liquid under study makes it possible to produce quasihydrostatic pressure with an extremely small shear component even when the liquid is solidified. An increase in pressure, as well as a decrease in temperature, results in the shift of the α peak to lower frequencies, and, in contrast to most glass formers, the absorption spectra in glycerol markedly change their shape [11, 12]. The shape of the absorption α peak below 1 GPa (Fig. 1a) is well described by the empiric Cole–Davidson formula [5]:

$$\varepsilon = \varepsilon_{\infty} + \Delta\varepsilon_{CD}/(1 + i\omega\tau_{CD})^{\beta_{CD}}. \qquad (1)$$

In the intermediate pressure range of 2–3 GPa (Fig. 1b), the approximation of the experimental data by formula (1) becomes much worse, and, above 3 GPa, the excess wing is transformed to the β peak (Fig. 1c). To model the dependences $\varepsilon(F)$ at $P >$ 3 GPa, we used the sum of expression (1) for the α-peak and the Cole–Cole formula [4],

$$\varepsilon = \Delta\varepsilon_{CC}/(1 + (i\omega\tau_{CC})^{\beta_{CC}}) \qquad (2)$$

to describe the shape of the β peak [15]. Note that at $2 < P < 3$ GPa, a strong broadening of the α peak is observed approximately up to four frequency decades. However, since the distance between the α and β peaks does not exceed two decades (Fig. 2a), the error of the fitting procedure sharply increases in this pressure range. The approximation of the spectra by formula (1) neglecting the contribution of secondary process (2) with increasing pressure results in a strong decrease in the parameter β_{CD} in relation (1), from $\beta_{CD} \sim 0.5$–0.55 at $P = 0.1$ MPa to $\beta_{CD} \sim 0.27$–0.34 at $P = 2.5$ GPa (see the insets in Figs. 1a, 1b). The baric coefficient for

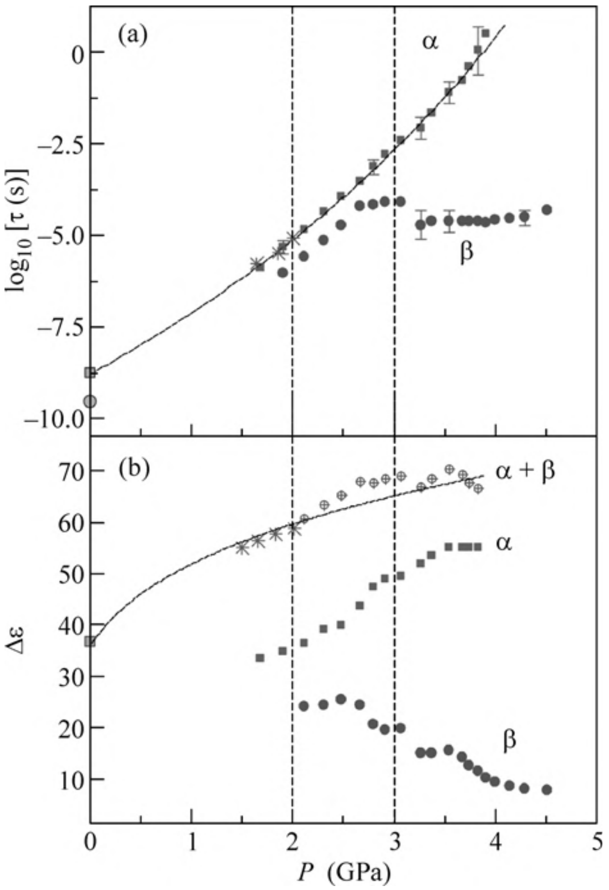

Fig. 2. Pressure dependences of the (a) time constant τ and (b) relaxation process strength $\Delta\varepsilon$ in Eqs. (1) and (2) used to approximate the isothermal ($T = 294$ K) spectra for the (squares) α and (circles) β processes. For comparison, the stars are the experimental data from [20]; the points at zero pressure are taken from [8, 15]. The lines are the approximation of $\tau_{CD}(P)$ and $\Delta\varepsilon(P)$ by the modified VFTH formula $\tau = \tau_0\exp[D/(P_0 - P)]$ [29] and the Tait law, respectively (see the discussion in the main text).

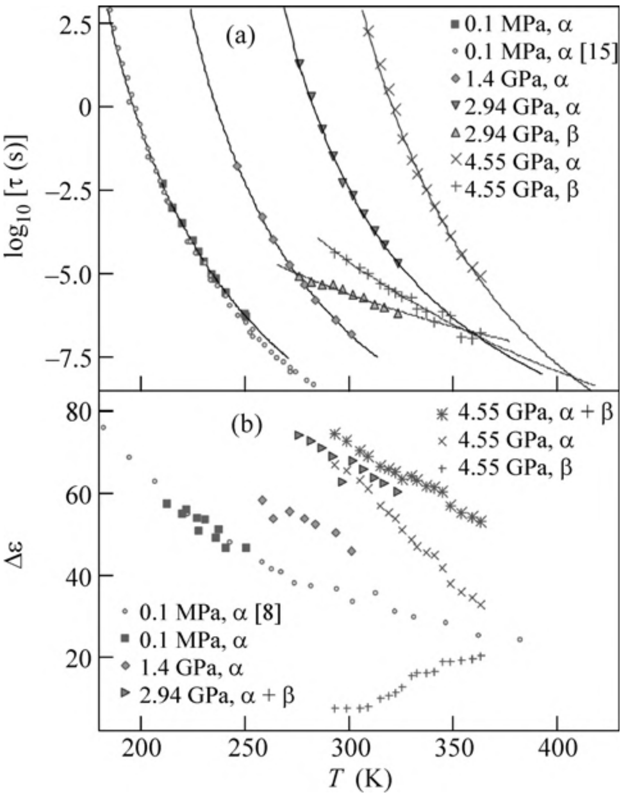

Fig. 3. Temperature dependences of the (a) time constant τ and (b) relaxation process strength $\Delta\varepsilon$ in Eqs. (1) and (2) used to approximate the isobaric spectra at different pressures for the α and β processes (see the notation in the figure). The points are the experimental data and the lines are the approximation of $\tau_{CD}(T)$ and $\tau_{CC}(T)$ by VFTH formula (3) and the Arrhenius law, respectively.

β_{CD} of about -0.1 GPa^{-1} agrees well with the value reported in [20] (-0.13 GPa^{-1}), and the use of the sum of two contributions (1) and (2) to model the spectra at pressures above 3 GPa results in higher values of $\beta_{CD} \sim 0.4$. This allows us to conclude that a considerable broadening of the absorption α peak in the intermediate range of 2–3 GPa, which corresponds to a decrease in β_{CD}, is a manifestation of the secondary relaxation.

Figure 3a presents the temperature dependences of the relaxation times τ_{CD}, τ_{CC} in Eqs. (1) and (2) at constant pressures of 0.1 MPa, 1.4 GPa, 2.94 GPa, and 4.55 GPa. According to this figure, the τ_{CD} (T, P = const) dependences at any pressure values are described well by the VFTH empiric relation [3]

$$\tau_{CD} = \tau_0\exp[DT_0/(T - T_0)]. \tag{3}$$

Determining the parameters in relation (3) from the experimental data, the isobaric fragility can be calculated as follows [31]:

$$M_P = \left.\frac{d\log(\tau_{CD})}{d(T_g/T)}\right|_{T = T_g} = \frac{DT_0T_g}{\ln(10)(T_g - T_0)^2}. \tag{4}$$

It is commonly accepted that the fragility depends on the energy landscape [32] and should correlate with various dynamic properties of the glass formers [22, 31, 32]. Moreover, this parameter makes it possible to quantitatively characterize the behavior of the structural relaxation time constant under varying ambient conditions and to compare different experimental results. The pressure dependences of the isobaric fragility m_P, the parameter T_0 in relation (3), and the glass transition temperature $T_g|_{\tau = 1000\text{ s}}$ calculated by the data presented in Fig. 3 are shown in Fig. 4 in comparison with the pressure dependences of T_g, T_0, and m_P taken from [17, 31, 33, 34]. It follows from Fig. 4 that our results within the measurement errors are in good quantitative agreement with the previously reported data.

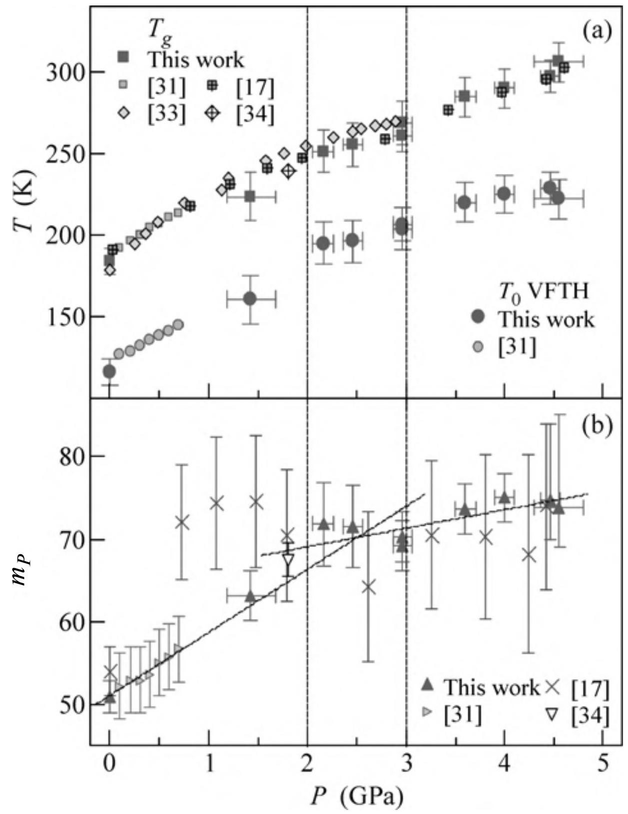

Fig. 4. Pressure dependences of the glass transition temperature T_g, the parameter T_0 in VFTH formula (3), and the fragility m_P. For comparison, the following data are also presented: T_g, T_0, and m_P from [31], T_g obtained from the measurements of viscosity under pressure from [33], T_g and m_P calculated in [17] by the data from [20] and (the point at 1.8 GPa) [34]. The lines in (b) are the least squares fits of the data from [31] for $P < 0.7$ GPa and our data for $P > 2.5$ GPa.

We notice that, in contrast to the rather smooth curves $T_g(P)$ and $T_0(P)$ shown in Fig. 4a, the behavior of the fragility $m_P(P)$ in Fig. 4b changes considerably in the intermediate pressure range of 2–3 GPa. However, the statement made in [17, 34] that the sharp increase in the fragility is changed beginning with a pressure of about 2 GPa to its constant value is not quite correct. First, it is easy to verify that, in the range of 2–3 GPa, the fitting of the spectra containing the contribution of the β peak, which is considerable in amplitude but close in frequency, by formula (1) neglecting relation (2) results in the systematic overestimation of the m_P values by about 10%, and this leads to a corresponding increase in the steepness of the initial region of $m_P(P)$. Second, a marked increase in m_P is also observed at pressures higher than 3 GPa.

We analyze the behavior of the temperature and pressure dependences of the parameters of model functions (1) and (2) (see Figs. 2, 3) in terms of the classification of the secondary relaxation processes proposed in [12]. The scenario where the excess wing in glycerol is the JG relaxation masked by a more intense α process close in frequency has been repeatedly discussed [10–13, 18]. In the case of the secondary JG-type relaxation, according to [12], the parameters of the α and β processes are related as $\tau_\beta(T, P) \sim \tau_0(T, P) = (t_c)^n(\tau_\alpha)^{1-n}$, where τ_α and n are the parameters of the Kolrausch function $\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}]$, which describes the time dependence of the α relaxation process; $t_c = 2$ ps; and τ_0 is the characteristic time of the primitive relaxation process in the Ngai model [11]. It was shown in [29] that this criterion (taking into account its approximate character) is satisfactorily valid for the temperature dependences $\tau(T)$, but the pressure dependence $\tau_{CC}(P)$ (see Fig. 2a) appears to be anomalously weak and is rather similar to the behavior of this parameter in tripropylene glycol [23], where a similar β process is classified as the pseudo-JG relaxation [12]. Meanwhile, in contrast to tripropylene glycol, the presence of the electrically active internal degrees of freedom in the glycerol molecule seems rather doubtful.

Despite the aforementioned problems, the behavior of the parameters $\Delta\varepsilon_{CD}(T, P)$ and $\Delta\varepsilon_{CC}(T, P)$, as well as of $\tau_{CD}(T, P)$ and $\tau_{CC}(T, P)$ (see Figs. 2, 3), points to the presence of a correlation between the α and β processes. When approaching the pressure (or temperature) range where both processes are close in frequency, their contributions to Δε become comparable in magnitude. For this reason, we can suggest that the same elements are involved in both processes; i.e., the observed β relaxation is in a certain sense actually the precursor of the structural relaxation. The pressure dependence of the total strength of both relaxation processes (see Fig. 2b) is most interesting. According to the Kirkwood formula [5, 20],

$$\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty = \frac{2}{9}(n_0^2 + 2)^2 \times \left(\frac{2\varepsilon_s}{2\varepsilon_s + n_0^2}\right)\left(\frac{\pi N \mu_0^2}{kTV}\right) g \sim \frac{\text{const}}{TV}, \tag{5}$$

where $V(P)$ is the molar volume relating to pressure by the Tait equation of state [16]. The curve in Fig. 2b is the approximation of the experimental data by the formula $\Delta\varepsilon_{CC}(P) + \Delta\varepsilon_{CD}(P) = c_1/V + c_2$, where c_1 and c_2 are the constants and $V(P) = V_0[1 - 0.091\ln(1 + P/0.328)]$ (the parameters in the Tait formula are taken from [16] for $T = 280$ K). The data in Fig. 2b imply that the increase in the total strength of both relaxation processes with pressure is most likely attributed to an increase in the density. The behavior of the temperature dependences $\Delta\varepsilon_{CC}(T) + \Delta\varepsilon_{CD}(T)$ (see Fig. 3b) also qualitatively agrees both with formula (5) and the data reported in [15].

To summarize, a crossover between two modes of the relaxation dynamics in glycerol under pressures has been revealed in this work. It was suggested earlier [10, 18, 22] that the anomalous properties of glycerol are determined by changes in the structure caused by the breaking of hydrogen bonds under high pressures and temperatures; however, in [34], with the reference to the results of the molecular dynamics simulation [35], an increase in the hydrogen bonding was supposed. Anyway, the key role of hydrogen bonds seems doubtless, and such features of the relaxation behavior as fragility, as well as existence and type of the secondary relaxation, reflect particular properties of the energy landscape. The application of high pressure in the gigapascal range makes it possible to modify the structure of a liquid at the potential energy scale corresponding to the characteristic energy of hydrogen bonds. Significant changes in the fragility, the broadening of the α peak, and the appearance of the secondary relaxation in glycerol under high pressure are most likely interconnected, which is supported by the fact that all these effects occur in the same pressure range starting from 2–3 GPa. In addition, one can suppose that in other similar glass formers without β peak in the dielectric spectra under ambient conditions, the secondary relaxation may be observed at sufficiently high pressure.

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