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Isothermal and high-pressure studies of dielectric relaxation in supercooled glycerol

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Abstract. Measurements of isothermal ($T = -28^\circ\text{C}$), high-pressure behaviour (up to 270 MPa) of complex electric permittivity in supercooled glycerol are presented. The observed peaks of α relaxation in absorption curves show increasing relaxation time τ with increasing pressure. The behaviour of τ can be reproduced by the pressure version of an Arrhenius relation or by a modified Vogel–Fulcher–Tammann equation. The data obtained can be superimposed by applying the scaling form used by Dixon *et al* 1990 *Phys. Rev. Lett.* **65** 1108.

1. Introduction

The most well known features of glass-forming materials are the non-Debye behaviour of the relaxation function (for the α process) and the dramatic increase in the characteristic relaxation time τ on cooling [1–5]. However, despite enormous experimental and theoretical efforts, there is still no generally accepted theory in this area of physics. This situation induces the need for new experimental facts. One possible source are high-pressure studies which offer another path for approaching the glassy state. Pressure studies, associated with density changes, are particularly efficient in liquids. Unfortunately, investigations of relaxation processes as functions of pressure in supercooled liquids are scarce [6–9]. This is undoubtedly associated with serious experimental problems arising in such research. They involve the application of a high-pressure technique with relatively low temperatures and special measurement procedures.

In this paper, the results of dielectric relaxation measurements on supercooled glycerol are presented. The extensive experimental data available for this material (see [1–5] and references therein) mean that it can be treated as an important reference point in the physics of glass-forming liquids. Some experimental results even refer to the pressure behaviour. In [8] the evolution of relaxation times from viscosity measurements were analysed (for isotherms above 0°C). Forsman [7] made preliminary tests on the pressure behaviour of dielectric relaxation for the $T = -15^\circ\text{C}$. The research presented here has been conducted for the $T = -28^\circ\text{C}$ isotherm and for pressures up to 270 MPa. The data obtained allowed us to discuss the pressure evolution of relaxation times and to test the scaling behaviour for the pressure path.

2. Experimental details

Measurements were performed using a pressure system with a specially designed measurement capacitor described in detail in our previous papers [10, 11]. It enabled the

total isolation of the tested sample from the medium delivering pressure (mixture of hexane and silicone oil); the sample was in contact with only stainless steel, Teflon and quartz. The pressure chamber was thermostatted with an accuracy better than 0.1 K. The temperature was measured by means of Keithley 195 A multimeter with a platinum resistor (A1 class; DIN 43 760; resolution, ± 0.01 K) located in the jacket of the chamber. Additionally, a copper–constantan thermocouple was placed inside the chamber. The pressure was measured with a Nova Swiss tensometric pressure meter with a resolution of ± 0.1 MPa.

Measurements of complex electric permittivity have been conducted by applying a Solartron 1260A impedance analyser which offered a constant resolution of five significant digits for the tested capacitance ($C_0 \approx 10$ pF). Glycerol (HPLC class; anhydrous; Fluka) was used without further purification. Data were analysed using ORIGIN 3.5 software (Microcal Inc). All errors are given as three standard deviations.

3. Results and discussion

Examples of the experimental data obtained are presented in figure 1. Each curve corresponds to a different pressure. Moreover we noticed that, at any pressures in the supercooled state, there is a distribution of relaxation times which may be described by the semiempirical Davidson–Cole [12] equation.

The experimental data on ε' and ε'' can be fitted well by this equation. Then the parameter α obtained at different pressures allows us to describe the modification of the relaxation time distribution. The exponent α , which describes the distribution of relaxation times, changes its value from about 0.63 ($p = 0.1$ MPa) to 0.57 ($p = 270$ MPa) (see the inset in figure 2). The fits were made not simultaneously for the real and imaginary parts of the susceptibility. Because ε' and ε'' are related by the Kramers–Kronig relation, therefore a fit to either should lead to the same result. However, some small discrepancies between the values of the same fitting parameters of ε' and ε'' were observed.

The pressure evolution of relaxation times, taken from the positions of the peaks of the absorption curves, is shown in the main part of figure 2. The almost linear dependence obtained on a semilog arithmetic scale suggests the application of the relation

$$\tau = \tau_A \exp\left(\frac{PV^*}{RT}\right) \quad (1)$$

introduced by Leyser *et al* [9] when analysing the spectrum of the specific heat for *o*-therphenyl (OTP). For isobaric temperature studies, equation (1) takes the form of the well known Arrhenius relation; so it can be treated as its pressure version. We found that $\tau_A = 5.5 \pm 0.2 \mu\text{s}$ (the activation time) and $V^* = 16 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ (the activation volume). In figure 2 the fit is shown by a solid line. In contradiction to the above-mentioned studies on OTP [9] the value of V^* coincides poorly with the molar volume of glycerol (about 70 cm^3). The applicability of equation (1) for glycerol (and OTP) can be associated with their inclusion in the group of strong glass formers [1].

Recent dielectric studies on iso-dibutylphthalate [11], which belongs to fragile glass-forming liquids, indicate the applicability in that case of the pressure analogue of the Vogel–Fulcher–Tammann (VFT) relation:

$$\tau = \tau_0 \exp\left(\frac{B}{\tilde{P}}\right) \quad (2)$$

with $\tilde{P} = P_0 - P$ and $B = \text{constant}$, where P_0 is a pressure of an ideal glass transition.

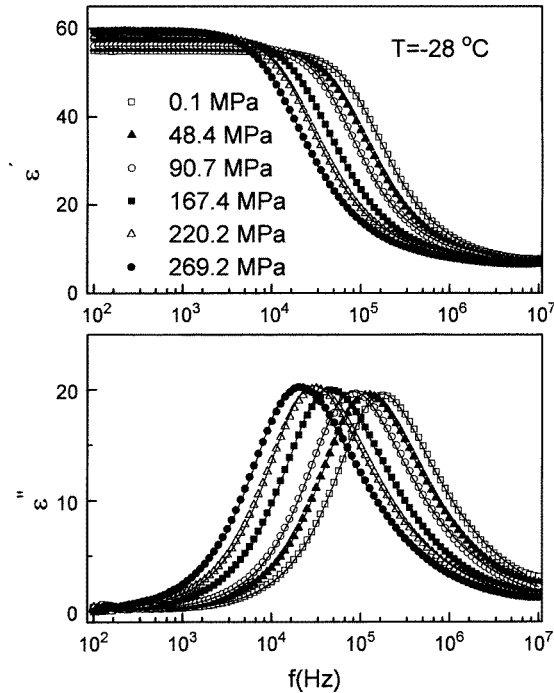


Figure 1. Experimental behaviour of ϵ' and ϵ'' in supercooled glycerol at the labelled pressures ($T = -28$ °C): —, Davidson–Cole fits.

This relation also allows us to reproduce reasonably obtained experimental data, particularly near glass transition pressures. The fit (broken line in figure 2) gave $B = 32\,800 \pm 600$ MPa and $\tau_0 = 2 \pm 0.1$ ps. The value $P_0 = 2200$ MPa has been approximated from pressure studies of viscosity [8]. It is worth mentioning that defining the distance from the characteristic pressure as $\tilde{P} = (P_0 - P)/P$ the same broken line in figure 2 is obtained. In this case the parameter $B = 14.9 \pm 0.4$ and $\tau_0 = 6 \pm 0.1$ μ s. The value of the pre-exponential factor τ_0 is close to that obtained using equation (1). This may be caused by the fact that $P_0 - P \approx \text{constant}$ for $P_0 \gg P$ and then equation (2) with the last definition of \tilde{P} reduces to equation (1). Moreover, on the other hand, it is easy to see that for $p \rightarrow 0$ the values of pre-exponential parameters are equal and they have the meaning of relaxation times at atmospheric pressure.

Similar normalization of the dimensionless distance from the singular point for a field thermodynamic variable has been successfully applied by Sengers *et al* [13] when analysing the anomaly of electric permittivity in critical solutions.

Recently, a form of universality was discovered by Dixon *et al* [14], who found that the dielectric relaxation data for several low-molecular-weight glass-forming liquids measured over a wide range of temperatures can be collapsed onto a single scaling curve when plotted as $w^{-1} \log[\epsilon'' f_p / (\Delta \epsilon f)]$ versus $w^{-1} (1 + w^{-1}) \log(f/f_p)$, where $\epsilon'' = \epsilon''(f)$ is the loss part of dielectric susceptibility, f the measuring frequency, $\Delta \epsilon$ the relaxation strength and w the half-width of the loss peak normalized to the corresponding half-width of the Debye peak. However, some workers [15–18] have pointed out the limitation in the validity of the scaling relationship proposed by Dixon *et al*. Comparing the dielectric data of low-

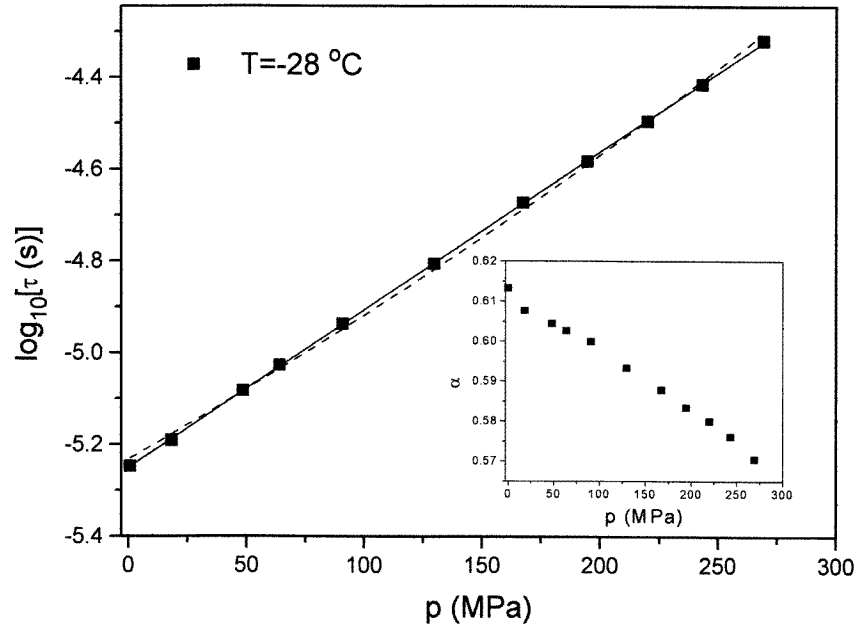


Figure 2. The pressure dependence obtained for relaxation times: —, equation (1); ---, equation (2). The inset shows the pressure variations in the exponent α in the Davidson-Cole relation.

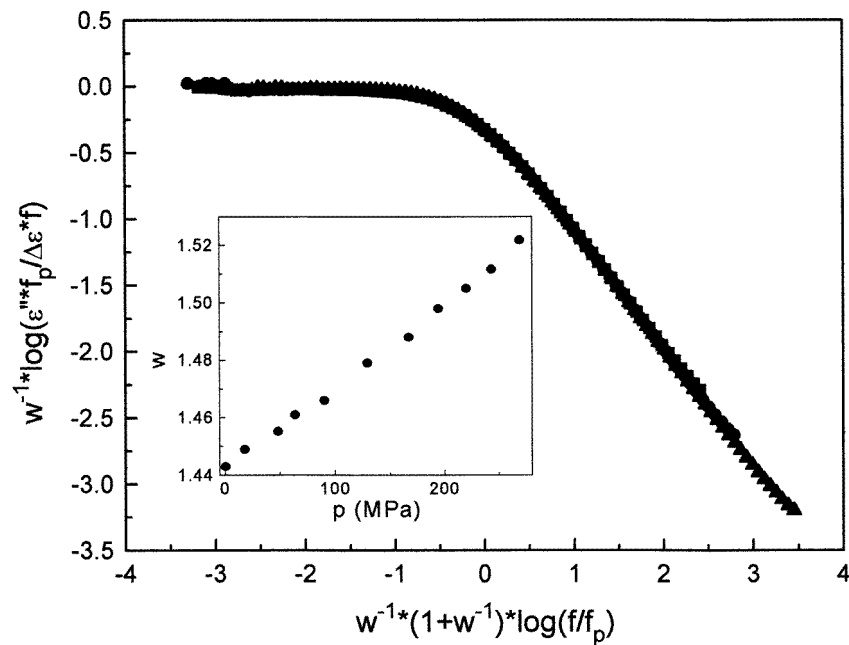


Figure 3. The scaling plot of Dixon *et al* [14] for the pressure data from figure 1.

molecular-weight systems and typical amorphous polymeric substances, Schönhals *et al* [15] showed that the above scaling form holds good when the low-frequency relaxation follows the power rule $\varepsilon'' \sim f^m$ for $f \ll f_p$ with $m = 1$, whereas it fails at low frequencies when $m < 1$.

In the case of absorption curves obtained in pressure measurements for glycerol the scaling form proposed by Dixon *et al* is fulfilled (the main part of figure 3). The full width W at half-maximum of absorption curves increases slightly with increasing pressure (the inset in figure 3). The values obtained for the exponents α , widths W of absorption curves and average relaxation times τ are collected in table 1.

Table 1. The values obtained for the relaxation times, Davidson–Cole exponent α and widths of absorption curves.

P (MPa)	τ (μ s)	α	W
0.1	5.66	0.613	1.443
18.2	6.45	0.607	1.449
48.4	8.28	0.604	1.455
64	9.41	0.602	1.461
90.9	11.5	0.6	1.466
129.6	15.6	0.593	1.479
167.4	20.7	0.587	1.488
194.7	25.9	0.583	1.498
220.2	31.1	0.58	1.505
243.3	38.5	0.576	1.5117
269.3	48	0.571	1.522

4. Conclusions

We have studied the pressure behaviour of the complex electric permittivity in supercooled glycerol ($T = -28^\circ\text{C}$). The behaviour of relaxation times has been discussed by means of pressure versions of the Arrhenius and VFT relations. Their applicability suggests the eventual equivalence of the isobaric temperature and isothermal pressure behaviours [11]. The pressure broadens the spectrum of relaxation times (increase in W and decrease in α). However, it influences only the right high-frequency wing of absorption curves.

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