Fragility of glycerol under pressure

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More than 30 years ago an outstanding paper on the dielectric properties of glycerol was published [1]. Since then much progress has been made in extending the frequency / temperature range. But measurements under elevated pressure are scarce. Based on the old data Paluch et al. asserted that there is an initial increase of the fragility, the slope at the glass transition temperature in the Angell plot, with pressure [2]. We constructed an apparatus to measure dielectric spectra under constant hydrostatic pressures up to 700 MPa and temperatures down to 130 K, limited by the freezing of the pressure transmitting fluid. Our set-up is similar to that described in [3].

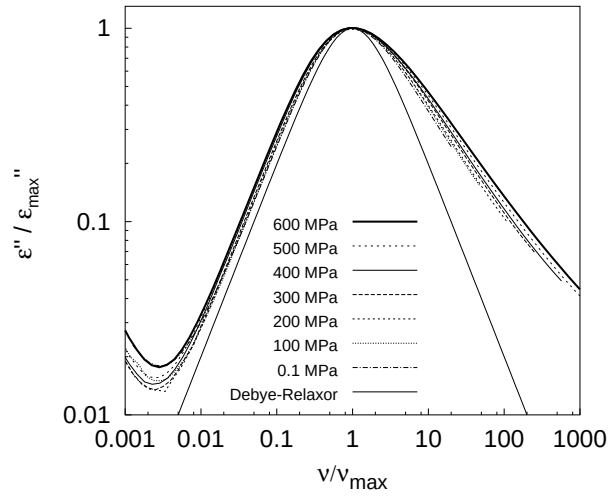

FIG. 1: Masterplot of the imaginary part of the dielectric permittivity for the structural relaxation of glycerol at 240 K for different pressures. Data points are omitted for clarity. The thin solid line describes a mono-exponential Debye process.

Fig. 1 shows the simple scaling – $\varepsilon''_{\max}$ decribes the maximum value of the dielectric loss at the frequency $\nu_{\max}$ – for 99.5% glycerol supplied from Aldrich at 240 K for different pressures in a double-log plot. The left wings are pressure independent and increase slightly sublinear with frequency, the slope of the high-frequency wing decreases with increasing pressure. Thus the FWHM of the curves gets broader by 16% between atmospheric pressure and 600 MPa.

In Fig. 2 we plotted $-\log 2\pi\nu_{\max}$ versus the T_g normalized reciprocal temperature. The glass transition temperature T_g for glycerol varies with pressure in a strongly nonlinear way, compared to other glass-formers, as shown in the inset. We defined T_g as the temperature where the maximum of the dielectric loss is at 1 mHz. The curves may be fitted by VFT equations with slightly increasing numerator in the exponent (D parameter) and pre-exponential factor increasing from 6 to $15 \cdot 10^{14}$ Hz with pressure. The fragility m, also called steepness index, is 54 ± 2

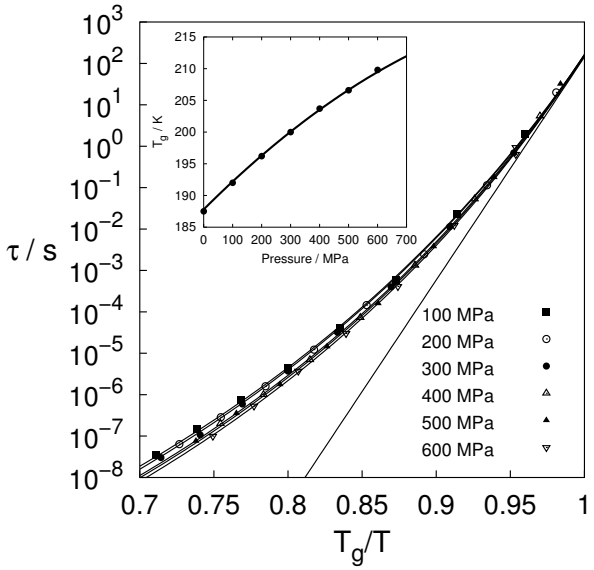

FIG. 2: Angell plot of the inverse peak frequency of dielectric spectra of glycerol for different pressures. The asymptote indicates the steepness index. Inset: Nonlinear pressure dependence of the glass transition temperature of 99.5% glycerol.

in our pressure range. This value coincides with the value given for atmospheric pressure [4] but is essentially lower than those derived at elevated pressures in [2]. One reason for the discrepancy may be their extrapolation of the data over an extended range, another the strongly nonlinear dependence of T_g with pressure. Interestingly T_g rises approximately linearly with a slope of 18 K/GPa at higher pressures, as measured by a ruby fluorescence technique up to 12 GPa [5]. We supposed that water content of glycerol might play a role. But our measurements of a 85% glycerol-water-mixture yielded the same masterplot and the same fragility as the 99.5% glycerol, merely T_g was lowered by about 10 K.

Concluding to a first approximation the fragility of glycerol derived from dielectric data is pressure independent like those of the few other fragile, small molecule glass-formers measured up to this day.

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