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Pressure-induced isothermal glass transition of small organic molecules

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We present a complete set of overlapping pressure-volume-temperature and dielectric relaxation data of the glass forming liquids propylene carbonate, meta-fluoroaniline, and glycerol under pressure up to 700 MPa. In all the samples a glass transition is induced by pressure at constant temperature. We compare the spectral shape of the structural relaxation process in the glass forming liquids with increasing pressure using a simple scaling for the maximum of the dielectric loss. Relaxation times measured at various temperatures and pressures can be scaled on a mastercurve by a single control parameter, the product of temperature and specific volume with a material-dependent exponent. This exponent exhibits the numerical value 4 for van der Waals liquids but is smaller for glass formers with hydrogen bonding.

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I. INTRODUCTION

Notwithstanding great experimental and theoretical efforts, the glass transition is still not understood.[1,2] The key question is the following: What drives the dramatic slowing down of structural relaxation? Most investigations of glass forming liquids concentrate on temperature effects at ambient pressure although there is a clear interest in a two-dimensional view of the glass forming process. Here, two-dimensional means the knowledge of the dynamical and static behavior of the liquid as a function of both temperature and pressure. Pressure and temperature affect the molecular mobility in different ways. While pressure yields a denser molecular packing and ultimately jamming, the primary effect of temperature is a trapping of molecules in potential wells of the energy landscape. Statements concerning the relative importance of thermal energy and free volume in glass forming liquids reach from “density is not the only variable” to “temperature is the dominant variable.”[3–5] Already Litovitz argued that both Eyring’s rate theory and free-volume theories have a fundamental error in that they neglect each other.[6] Since density also depends on temperature, isothermal measurements are wanted. Due to experimental problems in the isothermal variation of pressure at low temperatures, data are scarce for small molecule organic liquids with low glass transition temperatures (see, e.g., Refs. 7–9).

We have chosen three prototypical small-molecule organic glass formers: propylene carbonate ($C_4H_6O_3$), meta-fluoroaniline ($F\,C_6H_4NH_2$), and glycerol [$C_3H_5(OH)_3$]. All three materials are good glass formers, i.e., they resist attempts of crystallization. Propylene carbonate is a fragile van der Waals liquid with a caloric glass transition temperature $T_g = 156$ K at atmospheric pressure. The fragile liquid meta-fluoroaniline ($T_g = 173$ K) exhibits a tendency to form intermolecular hydrogen bonds.[10] The most extensively investigated hydrogen-bonded glycerol ($T_g = 188$ K) is of intermediate fragility, according to Angell’s nomenclature.[11] They were studied at elevated pressures using various techniques such as dielectric spectroscopy, calorimetry, and neutron scattering.[12–14] In this paper we present our volumetric and dielectric studies of propylene carbonate, meta-fluoroaniline, and glycerol under hydrostatic pressure up to 700 MPa at temperatures down to 200 K, i.e., we determined the equation of state and the isothermal structural relaxation dynamics.

II. EXPERIMENTAL

Our experiments have been carried out in a home-made CuBe pressure cell with an inner volume of about 14 mm diameter and 40 mm length. This volume was connected via a capillary with the computer-controlled pressure generator, a modified commercial high pressure pump. The pressure transmitting fluid was a 1:1 mixture of *n*-pentane and iso-pentane.[15] Thus pressure can easily be changed even at low temperatures at a rate of 1 MPa/min because it is necessary to avoid temperature changes in the samples. The cell is thermostatted to better than 0.1 K using an ethanol-methanol mixture or precooled nitrogen circulating around the cell. The temperature was measured both within the cell and on the outer surface of the cell with Pt100 sensors. The pressure dependence of the resistance of the Pt100 sensor was taken into account. The pressure sensor had a resolution of 0.1 MPa. Pressure and temperature could be adjusted simultaneously from atmospheric pressure up to 700 MPa down to 130 K, limited by the freezing of the pressure transmitting fluid with an accuracy of 0.5 MPa and 0.1 K, respectively. This offers an environment very suited to investigating the glass transition of small molecule glass formers.

The dilatometric setup is a home-made metal-bellow type (Fig. 1) which allows us to measure volume changes of the sample up to 30% with a relative accuracy of 0.1%. The readout of the dilatometer, i.e., the change of the length of the bellow, is done inductively with a differential transformer. Data taken at increasing and decreasing pressure completely coincide; no indication of a hysteresis due to the apparatus is observed. Using water as a reference, substance agreement with previous measurements[16] was found within 0.5% in the pressure range up to 700 MPa.

The dielectric measurements were carried out using a cylindrical capacitor made of stainless steel with a geometric capacity of 16.4 pF. The sample volume was separated from

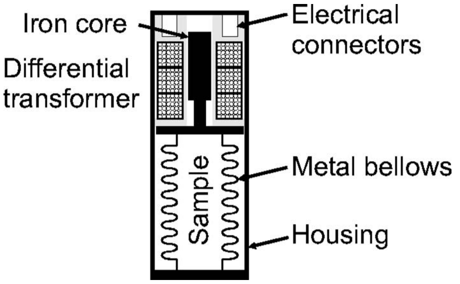

FIG. 1. Sketch of the metal-bellows dilatometer.

the pressure transmitting fluid by a PTFE membrane. Capacity and loss of the samples were measured with an impedance analyzer (Alpha from Novocontrol). The chemicals were purchased from Aldrich chemical company and measured as supplied. The purity was guaranteed to be higher than 99.5% in the case of propylene carbonate and glycerol and higher than 99% in the case of the colorless meta-fluoroaniline.

III. EQUATIONS OF STATE

First, we show the results of the static pressure-volume-temperature measurements. In Figs. 2–4, the pressure dependence of the relative volumes V/V_0 for propylene carbonate, meta-fluoroaniline, and glycerol is plotted, where V_0 is the sample volume at 280 K and 0.1 MPa.

All three samples exhibit the typical behavior of liquids at elevated pressures: (*i*) The compressibility decreases with increasing pressure. (*ii*) The compressibility is greater at higher temperatures. The curves of the strongly H-bonded glass former glycerol (Fig. 4) resemble those of propylene carbonate and meta-fluoroaniline, but show a smaller compressibility by a factor of about 2. In the case of meta-fluoroaniline (Fig. 3) and glycerol (Fig. 4), a purely isothermal glass transition can be observed at 200 K by a gradual break in slope in the investigated pressure range. Note that the mass density of the glass at 200 K and high pressures is lower than in the liquid at higher temperatures and the same pressures. Anticipating the dielectric results, an isothermal glass transition at 200 K is expected at 540 MPa in the case of propylene carbonate (Fig. 2).

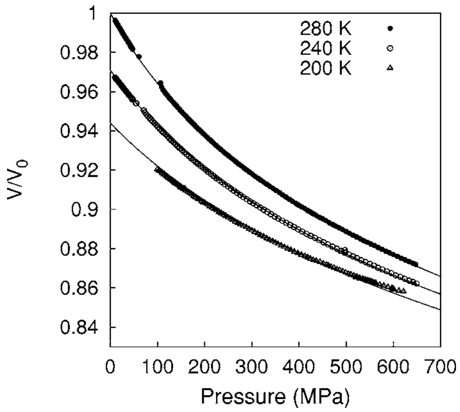

FIG. 2. Relative volume of propylene carbonate as a function of pressure at different temperatures. The lines are Tait fits.

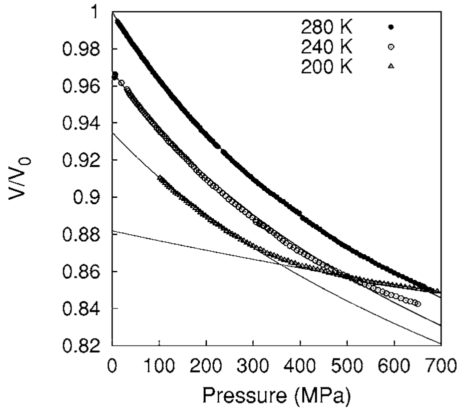

FIG. 3. Relative volume of meta-fluoroaniline as a function of pressure at different temperatures. The lines are Tait fits. At the lowest temperature, the kink indicates a purely pressure induced isothermal glass transition.

The data can be fitted using a generalized Tait equation[17]

$$\frac{V}{V_0}(p,T) = \frac{V}{V_0}(p_0,T)\left[1 - A_T \ln\left(1 + \frac{p}{B_T}\right)\right], \qquad (1)$$

where p and T are the absolute pressure and temperature, respectively, V_0 is the reference volume at 280 K and atmospheric pressure p_0, and A_T and B_T are fit parameters. In Table I we show the Tait-fit parameters for the three samples. The fits are excellent if the sample remains liquid in the whole pressure range. In the glassy state we need a different set of parameters (Table I). A_T is constant, independent of temperature. Usually a value of 0.0894 is used for different materials,[18] but we get a better fit if we assume a different value in the case of meta-fluoroaniline. B_T decreases linearly with temperature to a good approximation.

Thus we may write down the equation of state for proyplene carbonate

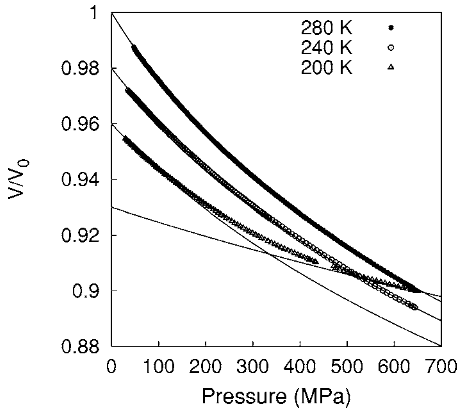

FIG. 4. Relative volume of glycerol as a function of pressure at different temperatures . The lines are Tait fits. The kink of the 200 K curve indicates a purely pressure-induced isothermal glass transition.

TABLE I. Fit parameters of the generalized Tait equation (1). Within the glassy state represented by the flatter part of the curves at 200 K in Figs. 3 and 4, a different set of parameters is needed, labeled by the addition (glass).

Substance	T(K)	$(V/V_0)(0,T)$	A_T	B_T(MPa)
propylene carbonate	280	1	0.091	208
	240	0.972	0.090	260
	200	0.944	0.090	339
meta-fluoroaniline	280	1	0.125	288
	240	0.968	0.129	350
	200	0.935	0.130	450
	200 (glass)	0.882	0.125	2000
glycerol	280	1	0.091	328
	240	0.981	0.096	427
	200	0.960	0.095	500
	200 (glass)	0.930	0.095	1600

$$\frac{V}{V_0}(p,T) = \exp[7.2 \times 10^{-4}(T-280)] \times \left[1 - 0.09 \ln\left(1 + \frac{p}{662 - 1.64T}\right)\right], \qquad (2)$$

with p in MPa and T in K. It is common to fit the temperature dependence of the volume with a polynomial and units in degrees Celsius, yielding incorrect values below 273 K.[13] In our investigated range the thermal expansion coefficient at atmospheric pressure is almost temperature independent, so we fit the temperature dependence of the volume with an exponential. The second part describes the influence of pressure on the volume. Comparing the pressure dependence with the equation of state given by Ref. 13 does not show a significant difference, though those data were taken with a commercial dilatometer working only up to 200 MPa and at higher temperatures.

The behavior of meta-fluoroaniline is almost similar to propylene carbonate despite of the different type of bonds. We get the following equation of state in the liquid range with p in units of MPa and T in K:

$$\frac{V}{V_0}(p,T) = \exp[8.2 \times 10^{-4}(T-280)] \times \left[1 - 0.129 \ln\left(1 + \frac{p}{748 - 1.65T}\right)\right] \qquad (3)$$

The equation of state for liquid glycerol can be calculated to

$$\frac{V}{V_0}(p,T) = \exp[5 \times 10^{-4}(T-280)] \times \left[1 - 0.095 \ln\left(1 + \frac{p}{935 - 2.15T}\right)\right]. \qquad (4)$$

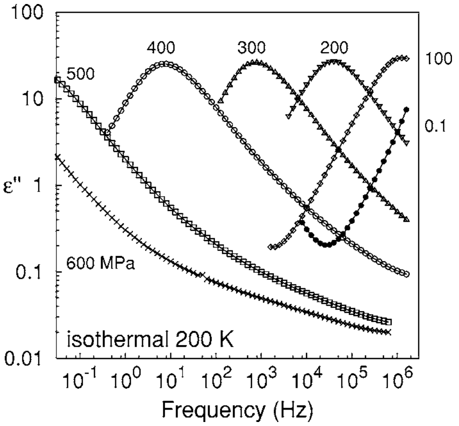

FIG. 5. Imaginary part ε'' of the dielectric function of propylene carbonate vs frequency for different pressures. The minimum at the lowest pressures is due to conductivity losses, the proximate rise to low frequencies is omitted for clarity.

A similar equation was given by Ref. 18, but their polynomial for the temperature dependence of the volume yields incorrect values below 273 K.

To summarize, the volumetric data tell us four main messages:

- The pressure dependence of the specific volume of the three liquids is very similar despite different types of interaction between the molecules.
- The equations of state can be fitted with generalized Tait equations in the pressure-temperature range of interest.
- An isothermal glass transition can be induced in all three systems.
- A glass can have a lower mass density than the corresponding liquid at high pressure.

IV. DIELECTRIC SPECTRA

In the following figures we exemplarily show dielectric spectra obtained at constant temperature with increasing pressure. To be more specific, we have measured capacity and dielectric loss angle of the capacitor filled with the glass-forming liquids at different temperature-pressure combinations and have calculated the dielectric function $\varepsilon = \varepsilon' - i\varepsilon''$. In Fig. 5, ε'' of propylene carbonate is plotted versus the measuring frequency in a double-logarithmic scale for various pressures.

The thermodynamic route corresponds to the 200 K curve of Fig. 2. Increasing pressure slows down the structural relaxation and shifts the relaxation peak through our frequency window. Above 500 MPa the frequency of the relaxation peak is found to be lower than 30 mHz, indicating that the liquid is near the glass transition. We shall define the glass transition as the point in the temperature-pressure plane where the frequency $\nu_{\max}$ of the α-relaxation peak equals 1 mHz. Of course, this definition is somewhat arbitrary, but this glass transition point coincides well with the calorimetrically defined glass transition. We extrapolate a glass-transition pressure $p_g(T)$ of (540 ± 20) MPa at 200 K assuming a Vogel Fulcher Tammann-analogous behavior of the peak frequency[12]

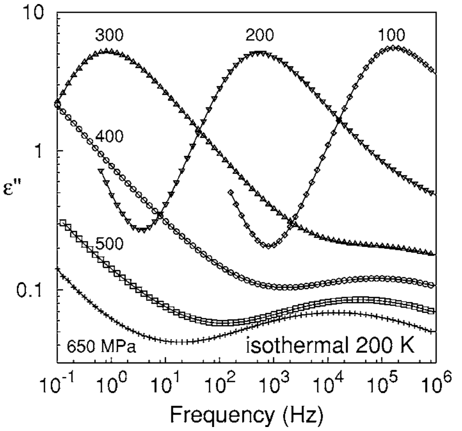

FIG. 6. Imaginary part ε'' of the dielectric function of meta-fluoroaniline vs frequency for different pressures. Increasing pressure shifts the relaxation peak to lower frequencies. In the glassy state, i.e., above 400 MPa, a pronounced, well-separated secondary relaxation peak is visible with an adumbration already at lower pressures.

$$\nu_{\max}(p) = \nu_{\mathrm{T}} \times \exp\left(\frac{-A \cdot p}{p_0 - p}\right). \tag{5}$$

A and p_0 are constants. ν_{T} is not an attempt frequency but the temperature-dependent frequency at which the maximum is observed at atmospheric pressure. The pressure dependence of the glass-transition temperature $T_{\mathrm{g}}(p)$ can be described by a second-order polynomial in the pressure range investigated in our experiment by

$$\begin{aligned} T_{\mathrm{g}}(p) = {} & (156.0 \pm 0.5)\mathrm{K} + (90 \pm 3) \cdot p\mathrm{K\ GPa}^{-1} \\ & - (13 \pm 1) \cdot p^2\mathrm{K\ (GPa)}^{-2}. \end{aligned} \tag{6}$$

Beside the α-relaxation peak, no further distinct relaxation peak is observed but a pressure-dependent wing is present on the high-frequency flank of the α peak.

The dielectric spectra of meta-fluoroaniline exhibit a pronounced β-relaxation peak with a larger spectral width and much smaller intensity than the α relaxation (Fig. 6). Both α and β relaxation show a pressure dependence, where that of the β process is much weaker than the pressure dependence of the α relaxation.[19] In this paper, we focus on the α relaxation. In meta-fluoroaniline the glass-transition temperature $T_{\mathrm{g}}(p)$ rises linearly with pressure up to 700 MPa to a good approximation

$$T_{\mathrm{g}}(p) = (173 \pm 1)\mathrm{K} + (82 \pm 2) \cdot p\mathrm{K\ GPa}^{-1}. \tag{7}$$

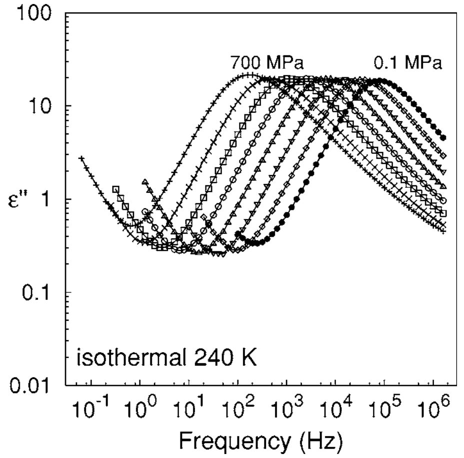

FIG. 7. Imaginary part ε'' of the dielectric function of glycerol vs frequency for different pressures. The influence of pressure on the α relaxation is much weaker than in propylene carbonate or meta-fluoroaniline.

Glycerol is known to exhibit no β-relaxation peak. The pressure dependence of the α relaxation is much weaker than in propylene carbonate and meta-fluoroaniline. Figure 7 shows the pressure dependence of the α-relaxation peak at 240 K. The thermodynamic route is the same as in Fig. 4 for the 240 K data. In this example, we stay in the liquid phase, to retain the α-relaxation peak in our frequency window for the whole pressure range. The pressure dependence of the glass-transition temperature $T_{\mathrm{g}}(p)$ is strongly nonlinear in the investigated range (0–700 MPa) and can be described by

$$\begin{aligned} T_{\mathrm{g}}(p) = {} & (188.3 \pm 0.5)\mathrm{K} + (47 \pm 2) \cdot p\mathrm{K\ GPa}^{-1} \\ & - (15 \pm 1) \cdot p^2\mathrm{K\ (GPa)}^{-2}. \end{aligned} \tag{8}$$

Interestingly, T_{g} rises approximately linearly with a slope of 18 K GPa^{-1} at higher pressures, as measured by a ruby fluorescence technique up to 12 GPa,[20] suggesting that Eq. (8) cannot be extended to pressures above 1 GPa.

V. SPECTRAL SCALING

To analyze the spectral shape one can use empirical fits such as Havriliak-Negami functions.[21] We simply compare the three glass-forming liquids by scaling the data onto the maximum of the absorption peak. In Fig. 8 such a double-logarithmic masterplot is shown for propylene carbonate, where $\varepsilon''_{\max}$ describes the maximum of ε'' at the frequency $\nu_{\max}$. The left wings are hardly pressure dependent and increase slightly sublinearly with frequency. The slope of the high-frequency flank decreases with increasing pressure. An

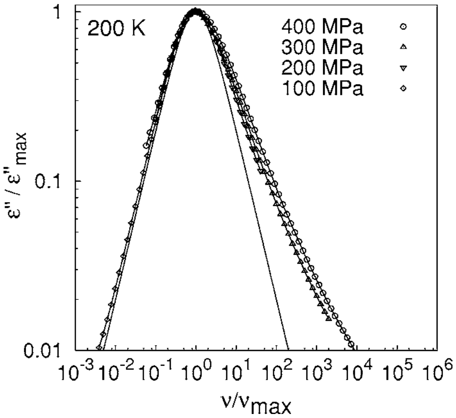

FIG. 8. Normalized α-relaxation curves of propylene carbonate shown in Fig. 5 as a function of relative frequency in a double-logarithmic plot. The behavior of a simple Debye relaxor is given by the solid line without symbols.

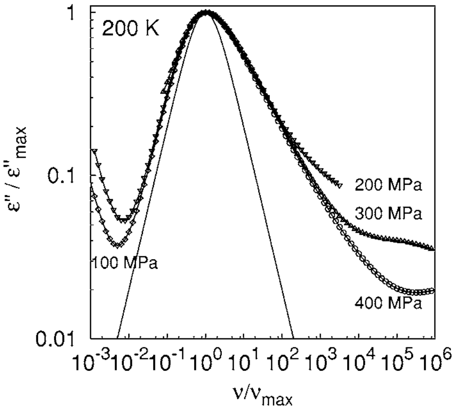

FIG. 9. Normalized α-relaxation curves of meta-fluoroaniline shown in Fig. 6 as a function of relative frequency in a double-logarithmic plot. The behavior of a simple Debye relaxor is given by the solid line without symbols.

even stronger pressure dependence can be observed in Fig. 5 for the high-frequency excess wing at the highest pressures where we do not catch the maximum of the dielectric loss in our frequency window.

Such a broadening is not observed in the case of meta-fluoroaniline (Fig. 9). Instead, a shoulder evolves from the high-frequency wing due to the better separation of the β process from the α process with increasing pressure.

The behavior of glycerol (Fig. 10) is similiar to that of propylene carbonate. Again the left wings hardly depend on pressure and increase slightly sublinearly with respect to frequency. The slope of the high-frequency flank decreases with increasing pressure.

It is tempting to assume that the observed broadening in propylene carbonate and glycerol has its origin in an underlying β relaxation spectrally located very close to the α process. This picture is supported by ageing experiments[22] not discussed here. Similar conclusions were drawn by Ref. 23, though they find no broadening in propylene carbonate at 1.78 GPa and 274 K.

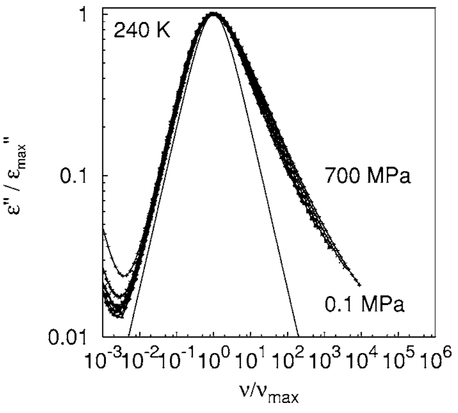

FIG. 10. Normalized α-relaxation curves of glycerol shown in Fig. 7 as a function of relative frequency in a double-logarithmic plot. Pressure slightly broadens the spectral shape of the α-relaxation peak. The behavior of a simple Debye relaxor is given by the solid line without symbols.

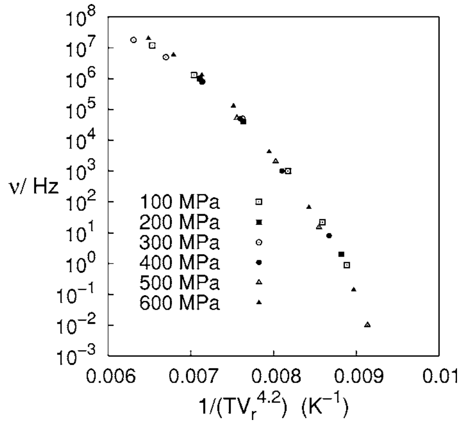

FIG. 11. Temperature-volume scaling of the α-relaxation peak of propylene carbonate. Plotting the logarithmic peak frequency as a function of $1/(TV_r^{4.2})$ one gets a mastercurve for all pressure-temperature combinations, where $V_r = V(p,T)/V(0.1\ \text{MPa}, 280\ \text{K})$ is a relative volume.

VI. TEMPERATURE-VOLUME SCALING

Without doubt the common route to form a glass is cooling a liquid. As shown in the previous sections, glasses can be formed by isothermal compression, too. Furthermore, we were able to produce glasses isochorically. This can be achieved by starting from a high temperature and a high pressure by cooling down and releasing the pressure simultaneously. So, neither temperature nor density or pressure alone are driving the glass transition. One can invert the question starting from the solid. How does a glass melt? Ross[24] introduced a generalized Lindemann melting law which was based on the assumption that melting should occur whenever the effective free volume available to a molecule reached a certain fraction of the molecular volume. For a rigorous free-energy calculation the structure and the forces between the molecules must be known. It is usual to assume that the structure (i.e., the distribution of particles) is determined by the repulsive forces alone.[25] For spherical inverse power potentials the Helmholtz free energy does not depend on volume and temperature separately, but only on the single variable Γ (Refs. [26] and [27]), definable by

$$\Gamma = \frac{1}{TV_r^w}, \tag{9}$$

where T is the temperature and $V_r = V/V_0$ the relative volume. V_0 is the volume at 280 K and atmospheric pressure, and $3w$ is the exponent of the repulsive potential. Historically, w was fixed to a value of 4 according to the exponent $3w=12$ of Lennard-Jones repulsion. Recently, it has been assumed that w is an adjustable parameter.[18,28] In Fig. 11 we apply this Γ scaling with adjustable w to propylene carbonate. The dielectric measurements were carried out isobarically at temperatures above 200 K and pressures between 100 and 600 MPa. Taking $w=4.2$, all relaxation frequencies are scaled onto a mastercurve. The estimated error of w is 0.2. Similarly, the value $w=3.7$ was derived from a combined analysis of dc conductivity data and dielectric relaxation times measured at

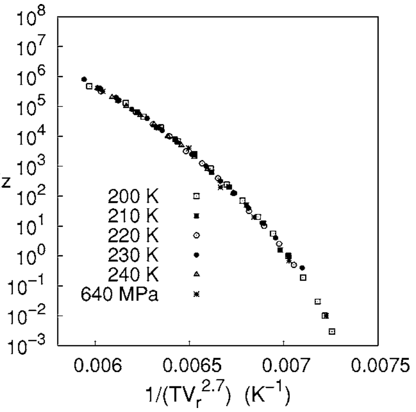

FIG. 12. Temperature-volume scaling of the α-relaxation peak of meta-fluoroaniline. The logarithmic peak frequency as a function of $1/(TV_{\mathrm{r}}^{2.7})$ are scalable onto a mastercurve for all pressure-temperature combinations with the relative volume $V_{\mathrm{r}} = V(p,T)/V(0.1\ \mathrm{MPa}, 280\ \mathrm{K})$.

283 K and higher pressures.[13] Thus, propylene carbonate behaves as expected like a van der Waals liquid with Lennard-Jones repulsion.

As already mentioned, meta-fluoroaniline exhibits a tendency to form intermolecular hydrogen bonds.[7,10] In Fig. 12 we have plotted data obtained by isothermal compression at 200, 210, 220, 230, and 240 K and data obtained by an isobaric experiment at 640 MPa. In this case an exponent of $w=2.7\pm0.2$ is derived. The scaling is strikingly good. Clearly, it is not important whether isobaric or isothermal routes are used in the ergodic liquid state.

Glycerol is the system among the three substances which has strong H bonds. The dielectric measurements were carried out isobarically at temperatures down to 200 K and pressures between 100 and 700 MPa (Fig. 13). It is not astonishing that $w=1.4\pm0.2$ deviates significantly from the exponent expected for a van der Waals system. Comparing this exponent with recent scalings of Dreyfus *et al.*,[18] who obtain $w=1.8$ for viscosity data between 273 K and 348 K, we find a good agreement. It should be emphasized that we did no extrapolation of either relaxation data nor volume to higher pressures or lower temperatures than indicated.

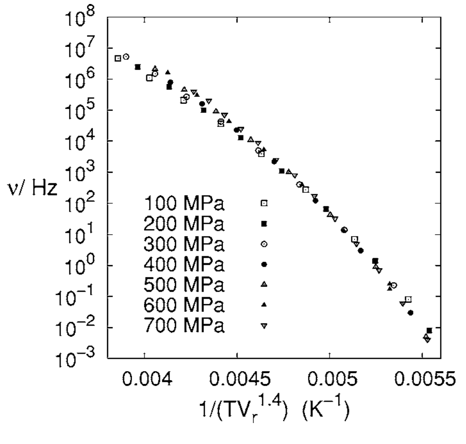

FIG. 13. Temperature-volume scaling of the α-relaxation peak of glycerol. The logarithmic peak frequency as a function of $1/(TV_{\mathrm{r}}^{1.4})$ scale onto a mastercurve for all pressure-temperature combinations. $V_{\mathrm{r}}=V(p,T)/V(0.1\ \mathrm{MPa}, 280\ \mathrm{K})$ is a relative volume.

As mentioned above, $3w$ is the exponent of the repulsive part of the molecule-molecule interaction potential. Therefore, a replusion exponent of 8.1 is expected for meta-fluoroaniline and 4.2 for glycerol. It seems to be contradictory that glycerol, the most incompressible liquid among the three samples, should have the softest repulsive potential. Furthermore, the almost equally compressible liquids propylene carbonate and meta-fluoroaniline show different exponents. The difference between the last two substances is the type of bond. Propylene carbonate has van der Waals interactions, which should be nondirectional. Meta-fluoroaniline has H bonds, an accordingly directed bond. Spherical symmetry seems to be non-negligible.

Some recent papers have already dealt with the Γ scaling. For the van der Waals liquid ortho-terphenyl ($T_{\mathrm{g}}=243$ K at atmospheric pressure), Tölle *et al.* reported $w=4$, obtained from the analysis of incoherent neutron scattering data in a limited time domain at pressures up to 240 MPa.[29] In accordance, $w=4$ and $w=4.25$ was derived for orthoterphenyl analyzing dielectric relaxation data over an extended frequency range by Refs. [18] and [28]. These two papers also report values between $w=1.9$ and $w=8.5$ for a couple of glass-forming polymers. Polychlorinated biphenyls with increasing chlorine content were fitted by $w=5.5$ up to $w=8.5$.[30] An astonishingly low value $w=0.13$ was found for sorbitol $[\mathrm{C_6H_8(OH)_6}]$ ($T_{\mathrm{g}}=267$ K at atmospheric pressure), a multilaterally hydrogen-bonded glass former with a pronounced β relaxation.[28] While it is imaginable that the repulsive part of the potential is steeper than $1/r^{12}$, with the limiting case $w\rightarrow\infty$ for hard spheres, it cannot be accepted that $3w=0.39$ is meaningful with respect to this power. The explanation for this unusual value is that w is also a measure for the importance of thermal energy. The scaling parameter w is lower for glass formers in which temperature is the more dominant control variable. $w=0$ describes a pure thermally activated process.

In hydrogen-bonded liquids clustering phenomena play an important role.[31] For water it has been accepted for a long time that the monomer species of the liquid form oligomers such as dimers, trimers, etc. The hydrogen bonding has been modeled as being analogous to chemical reaction equilibria described by Eyring's rate theory. The equilibrium constants are temperature and pressure dependent. In fact, hydrogen-bonded clusters have been detected via elastic neutron scattering in the case of meta-fluoroaniline, too.[10] Moreover, we rationalized the pressure dependence of the β-relaxation peak in meta-fluoroaniline by the assumption of two different species of clusters.[19] The ratio of the two species is fixed when leaving the ergodic regime. Crossing the glass transition line at lower temperatures yields bigger clusters and thus less dense packing of the glass. Summing up, it is probable that the w exponent of the Γ scaling is not only a measure for the repulsive part of the molecule-molecule interaction potential but also for the intermediate range order, i.e., the formation of clusters or, generalized, heterogeneity within the liquid or glass.

VII. CONCLUSION

We induced a transition into the glassy state at constant temperature by applying pressure to the organic liquids propylene carbonate, meta-fluoroaniline, and glycerol. The dielectric spectra measured at various pressures in the ergodic regime were scaled onto the maximum of the absorption peak. The low-frequency flank of the α peak is not affected by pressure. The spectral broadening on the high-frequency side of the α-relaxation peak in propylene carbonate and glycerol seems to have its origin in an underlying β process with a weak pressure dependence. The knowledge of the equation of state and of the temperature-pressure dependence of the α-peak frequency enables us to test the Γ scaling: As a function of $\Gamma=1/(TV^w)$, where w is a material-dependent constant, for each substance the relaxation peak frequencies lie on a master curve. This is achieved by using the measured data without anticipating the temperature-pressure-time superposition principle for conditions for which experiments are difficult. The result of the Γ scaling is strikingly good in the experimentally covered frequency range of about nine orders of magnitude. The explanation based on the repulsive part of the intermolecular potential alone is not convincing. To describe associated liquids, a quasichemical theory with pressure- and temperature-dependent equilibria of molecule clusters and spatial heterogeneity has to be taken into account. This explains naturally why the mass density of the glass at a certain temperature and high pressures is lower than in the liquid at higher temperatures and the same pressures.

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