

In search of invariants for viscous liquids in the density scaling regime:

Investigations of dynamic and thermodynamic moduli

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Supporting Information

Details of Experimental and Numerical Methods

To analyze dynamic and thermodynamic moduli discussed in the main part in case of glass-forming liquids, we have accurately calculated a few activation and thermodynamic quantities as well as some their ratios in different thermodynamic conditions selected at different constant pressures ($p=const$), constant volumes ($V=const$), and constant temperatures ($T=const$). The definitions of the quantities are given below, keeping the same numbering of them as that in the main part.

- The isochoric and isobaric activation energies, E_V^{act} and E_p^{act} , and the activation volume V_T^{act} ,

$$E_V^{act} = R(\partial \ln \tau / \partial (1/T))_V \quad (1)$$

$$E_p^{act} = R(\partial \ln \tau / \partial (1/T))_p \quad (2)$$

$$V_T^{act} = RT(\partial \ln \tau / \partial p)_T, \quad (3)$$

where R is the gas constant and the activation quantities are defined here by using a time scale τ of molecular dynamics.

- A so-called dynamic modulus in the standard temperature-pressure domain,

$$M_{p-T} = E_p^{act} / V_T^{act} \quad (4)$$

which was earlier suggested to correlate with the isothermal bulk modulus B_T defined as the inverse isothermal compressibility κ_T^{-1} ,

$$B_T = -(\partial \ln V / \partial p)_T^{-1}, \quad (5)$$

and a dynamic modulus considered by us in the temperature-volume domain,

$M_{V-T} = E_V^{act} / V_T^{act}$ as a proper alternative to Eq. (4) in search of invariants.

In our investigations, we have exploited the dielectric structural relaxation time as a time scale τ of molecular dynamics to calculate values of the activation quantities (Eqs. (1)-(3)), and consequently the dynamic moduli M_{p-T} and M_{V-T} . Since the broadband dielectric spectroscopy (BDS) measurements are typically carried out in isobaric or/and isothermal conditions, i.e., in the temperature-pressure (T - p) domain, a transformation of the dielectric data to the temperature-volume (T - V) domain has also required volumetric data, and their parametrization by an equation of state (EOS), which has provided the temperature-pressure dependence of volume, $V(T, p)$. Then, we have been able to calculate the thermodynamic modulus from Eq. (5), and determine the constant volume conditions needed to use Eq. (1).

We have studied three well-known van der Waals liquids, such as 1,1'-bis(p-methoxyphenyl)cyclohexane (BMPC), phenylphthalatein-dimethylether (PDE), and propylene carbonate (PC), which were measured by means of the BDS technique in their supercooled state at ambient pressure in the range of dozen decades of their structural relaxation times τ

and also at high pressure in some narrower ranges of τ . These dielectric data earlier reported in literature densely cover broad temperature ranges especially at ambient pressure, i.e., 242K – 320K for BMPC,^{26,27} 295K – 415K for PDE,^{28,29} and 159K – 371K for PC.³⁰

Thus, the isobaric activation energies could be calculated numerically from Eq. (2) along the ambient pressure isobar based on the experimental dependence $\tau(T)$ for each tested material. However, to evaluate the activation quantities defined by Eqs. (1) and (3), there are not such rich data sets collected in high pressure conditions in which the dielectric measurements are more complex and have more limitations than those at ambient pressure. Therefore, to thoroughly examine the values of the dynamic moduli M_{p-T} and M_{V-T} , which involve as follows:

- the isobaric activation energies calculated from Eq. (2) along an isobar of pressure p at given temperatures T_i ,
- the activation volumes evaluated from Eq. (3) at the same pressure p along the isotherms of the same temperatures T_i ,
- the isochoric activation energies calculated from Eq. (1) at the same pressure p along the isochores of volumes V_i found at the same temperatures T_i , i.e., $V_i = V(T_i)$,

we have applied the criterion for the power law density scaling,³¹

$$T_\tau V_\tau^\gamma = \text{const} \text{ at } \tau = \text{const}, \quad (6)$$

to generate high pressure isotherms, isochores, and isobars of structural relaxation times τ . It is worth noting that the density scaling criterion is usually also valid along the T_g -line and at any $\tau = \text{const}$ to a good approximation for real materials independently of applied units of τ (i.e., not only reduced units of the isomorph theory^{32,33} but also simply seconds).^{34,35,36} It should be emphasized that the suggested procedure is not only very useful, but also allows us to avoid using any other models to approximate the temperature-pressure dependences

$\tau(T, p)$ established from the BDS measurements. Thus, this procedure offers some kind of numerical experiment, the results of which enable to supplement the measurement data if the density scaling criterion given by Eq. (6) is satisfied to a good approximation at each τ in the analysis range.

It should be emphasized that it is reasonable to employ Eq. (6) in case of all the tested supercooled liquids, because each of them very well obeys the power density scaling law with the scaling exponent γ being a material constant independent of thermodynamic conditions as shown in literature with $\gamma=8.0$ for BMPC,³⁷ $\gamma=4.42$ for PDE,³⁷ and $\gamma=3.7$ for PC.³⁰ To determine the volume V as a function of T and p in Eq. (6), we have also employed pVT measurement data and their parametrizations in terms of the equations of state (EOSs), which were used to find the values of the scaling exponent γ for these materials. Thus, we have exploited the Tait EOS³⁸ parameterized for PC³⁰ and another EOS recently derived^{39,40,41} for supercooled liquids and parametrized for PDE,³⁹ and BMPC.⁴²

Exploiting Eq. (6), we have been able to generate high pressure isotherms of structural relaxation times τ at each temperature at which τ were determined from the BDS measurements at ambient pressure as well as high pressure isochores of structural relaxation times τ at each volume found from an EOS at each temperature at which τ were determined from the BDS measurements at ambient pressure. Then, it was possible to numerically calculate the activation quantities defined by Eqs. (1)-(3), and consequently yield the values of the dynamic moduli M_{p-T} and M_{V-T} along the ambient pressure isobar. In the next step, we have generated a high pressure isobar of structural relaxation times τ at $p=100\text{MPa}$ by finding temperatures from Eq. (6) at $p=100\text{MPa}$, which yield the same structural relaxation times τ as those determined from the BDS measurements at ambient pressure. Then, we have been able to repeat the procedure of the generation of isotherms and isochores of the structural relaxation times τ taking the high

pressure isobar $\tau(T)$ at $p=100\text{MPa}$ as a reference. As a consequence the dynamic moduli could be numerically calculated along the high pressure isobar at $p=100\text{MPa}$.

To illustrate the generation procedure, we show below its details using PDE as an example.

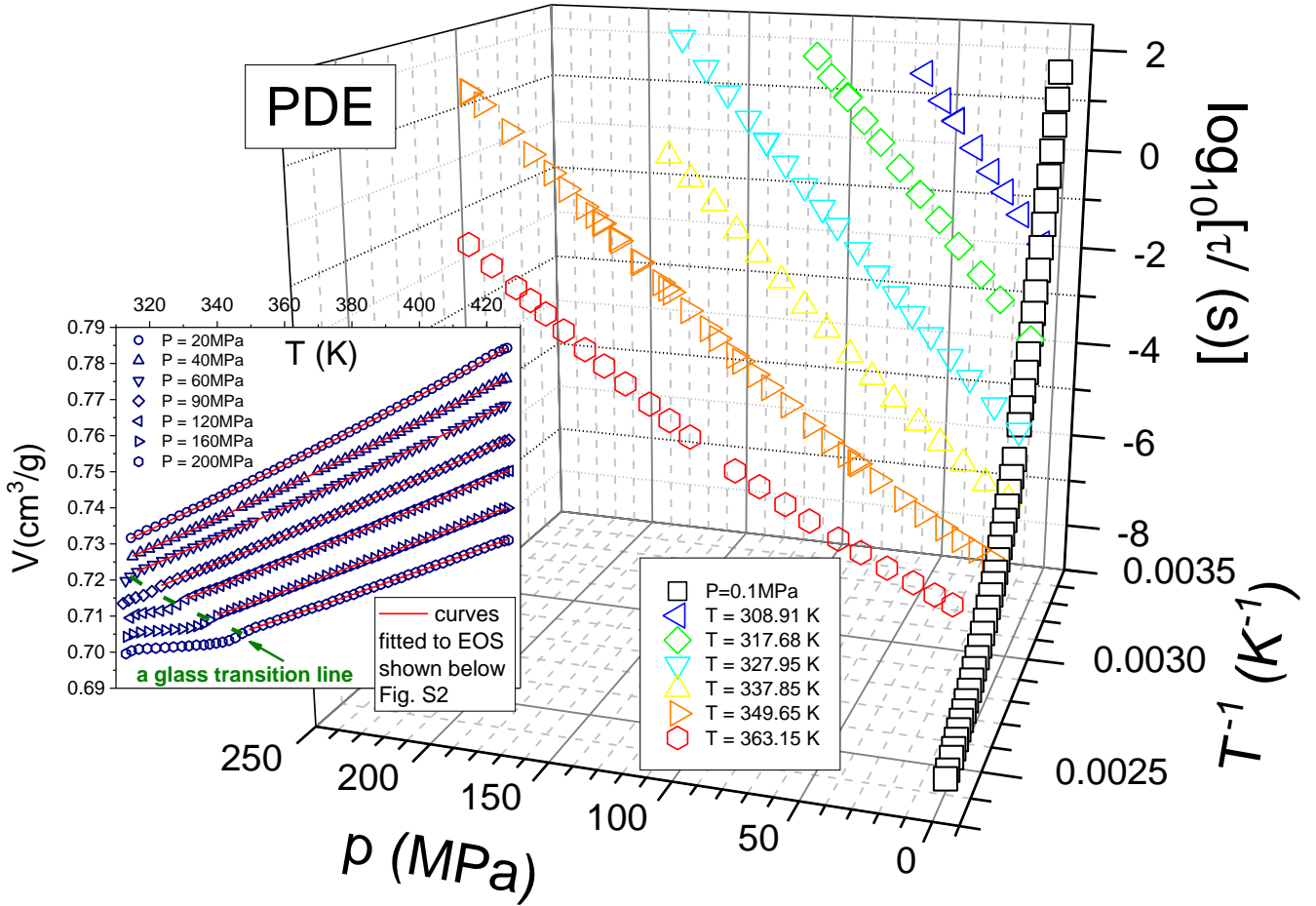


Fig. S1

The main panel demonstrates the temperature-pressure dependence of structural relaxation times earlier determined²⁸ from dielectric measurement data of PDE. In the inset, pVT measurement data²⁹ are shown using open symbols, while solids lines denote fitting curves to the EOS with its fitting parameters established earlier³⁹ and also presented below Fig. S2.

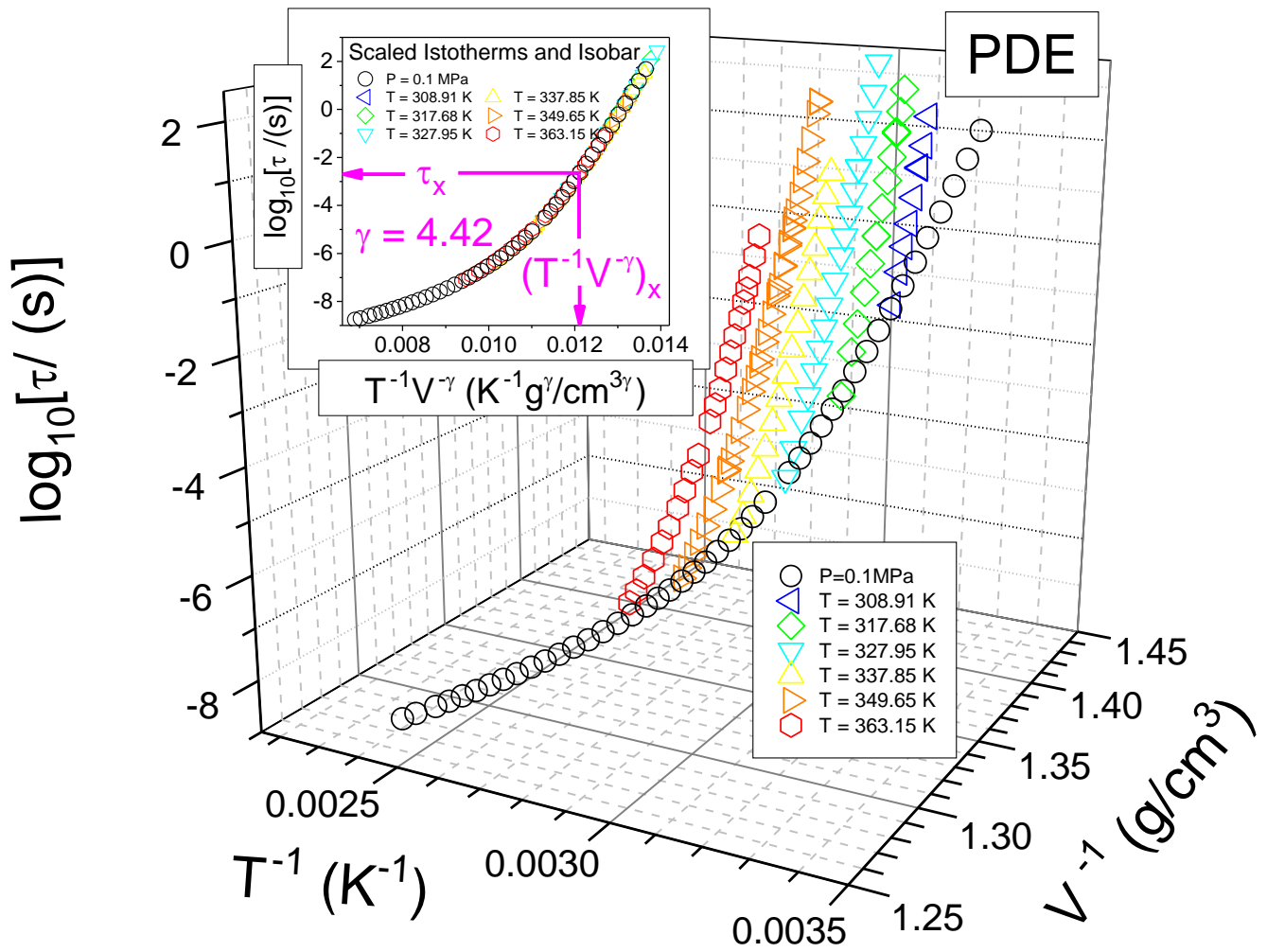


Fig. S2

The main panel demonstrates the temperature-volume dependence of structural relaxation times transformed from the original temperature-pressure dependence (shown for PDE in the main panel of Fig. S1) by using the EOS presented below and parametrized earlier for the supercooled liquid state.³⁹ The inset illustrates a perfect density scaling of structural relaxation times with the scaling exponent $\gamma=4.42$.³⁷

In the main panel of Fig. S1, there are presented six high pressure isotherms and ambient pressure isobar of the structural relaxation times τ earlier determined²⁸ directly from the BDS measurements. In the inset in Fig. S2, there are pVT measurement data also earlier reported²⁹ as well as their fit to the following EOS

$$V(T, p) = \frac{A_0 + A_1(T - T_0) + A_2(T - T_0)^2}{\left[1 + (p - p_0)(\gamma_{EOS} / B_{T_0}(p_0)) \exp(b_2(T - T_0))\right]^{1/\gamma_{EOS}}} \quad (\text{EOS})$$

with its fitting parameters $A_0=(0.72963 \pm 0.00004) \text{cm}^3/\text{g}$, $A_1=(4.37 \pm 0.01) \times 10^{-4} \text{cm}^3/(\text{gK})$, $A_2=(4.85 \pm 0.07) \times 10^{-7} \text{cm}^3/(\text{gK}^2)$, $B_{T_0}(p_0)=(2785 \pm 6) \text{MPa}$, $b_2=(4.26 \pm 0.02) \times 10^{-3} \text{K}^{-1}$, $\gamma_{EOS}=9.51 \pm 0.04$, which have been previously established³⁹ for the supercooled liquid region on the assumption of the fixed reference state, $T_0=298 \text{K}$ at $p_0=0.1 \text{MPa}$. In this way, we have parametrized the experimental dependences $V(T, p)$ and we have easily calculated the values of the thermodynamic modulus (the bulk modulus) B_T from Eq. (5). Moreover, we have been able to transform the dependence $\tau(T, p)$ to the T - V domain as shown in the main panel of Fig. S2. An important result of the initial stage of the analysis is a perfect density scaling of isothermal and isobaric experimental dependences $\tau(T, V)$ in terms of a single scaling variable $T^{-1}V^{-\gamma}$ with the earlier reported³⁷ value of the scaling exponent, $\gamma=4.42$, which has been depicted in the inset in Fig. S2.

A key point of the generation procedure is the fact that the value of the single variable $(T^{-1}V^{-\gamma})_x$ is a constant at a given structural relaxation time τ_x as illustrated in the inset in Fig. S2. In other words, $(T^{-1}V^{-\gamma})_x$ is a structural relaxation time dependent constant $C(\tau_x)$. However, a unique value $(T^{-1}V^{-\gamma})_x$ can be achieved by different combinations of T and V , as well as p via the dependence $V(T, p)$.

To generate an isotherm at $T=const$, we have found p_x from the equation $T^{-1}V^{-\gamma}(T, p_x) = (T_i^{-1}V^{-\gamma}(T_i, p_0))_x$ for each $(T_i^{-1}V^{-\gamma})_x$, corresponding to $\tau_x = \tau_i$ determined from the BDS measurements at T_i at ambient pressure p_0 . In this way, the isotherms have been plotted at each T_i in Fig. S3 and used to numerical calculations of the activation volumes at p_0 . It is worth noting that the isotherms have been generated also slightly below p_0 only to improve the accuracy of the numerical differentiation at p_0 , which has provided accurate values V_T^{act} at p_0 from Eq. (3).

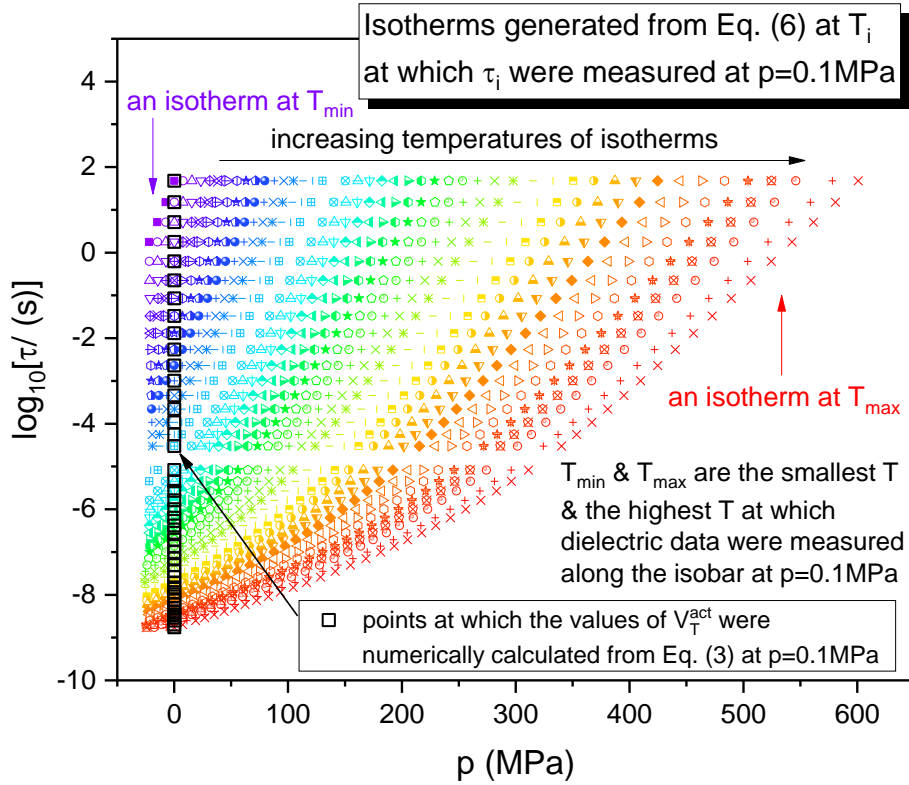


Fig. S3

The pressure dependences of the high pressure isotherms generated from Eq. (6) at each temperature at which the structural relaxation times (denoted by open black squares) were measured at ambient pressure.

To generate an isochore at $V=const$, where $V=V(T,p_0)$ is determined from EOS at a temperature T at ambient pressure p_0 , we have found T_x from the equation $T_x^{-1}V^{-\gamma} = (T_i^{-1}V^{-\gamma}(T_i, p_0))_x$ for each $(T^{-1}V^{-\gamma})_x$, corresponding $\tau_x = \tau_i$ determined from the BDS measurements at T_i at ambient pressure. In this way, the isochores have been plotted at each $V_i=V(T_i, p_0)$ in Fig. S4 and used to numerical calculations of the isochoric activation energies at p_0 . Similarly as isotherms, the isochores have been generated also slightly below p_0 to improve the accuracy of the numerical differentiation at p_0 , which has provided accurate values E_V^{act} at p_0 from Eq. (1).

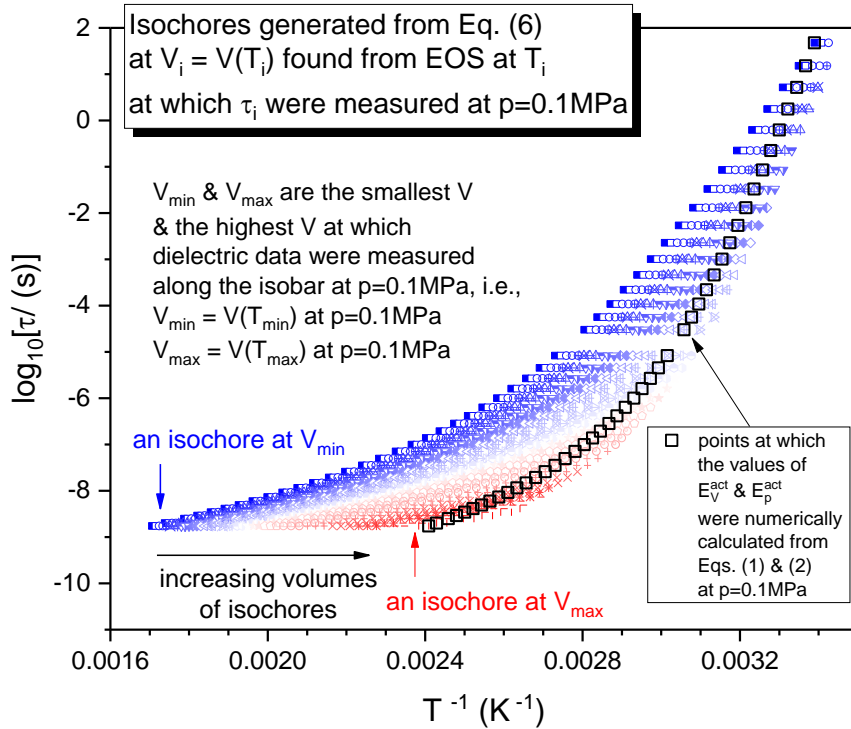


Fig. S4

The temperature dependences of the high pressure isochores generated from Eq. (6) at volumes found at each temperature at which the structural relaxation times (denoted by open black squares) were measured at ambient pressure.

To generate an isobar at $p=const$, we have found T_x from the equation $T_x^{-1}V^{-\gamma}(T_x, p) = (T_i^{-1}V^{-\gamma}(T_i, p_0))_x$ for each $(T^{-1}V^{-\gamma})_x$, corresponding $\tau_x = \tau_i$ determined from the BDS measurements at T_i at ambient pressure. In this way, the isobar at $p=100\text{MPa}$ has been plotted to constitute a reference for further calculations of the activation quantities from Eqs. (1)-(3) at $p=100\text{MPa}$ in analogous ways to those described above for $p_0=0.1\text{MPa}$.

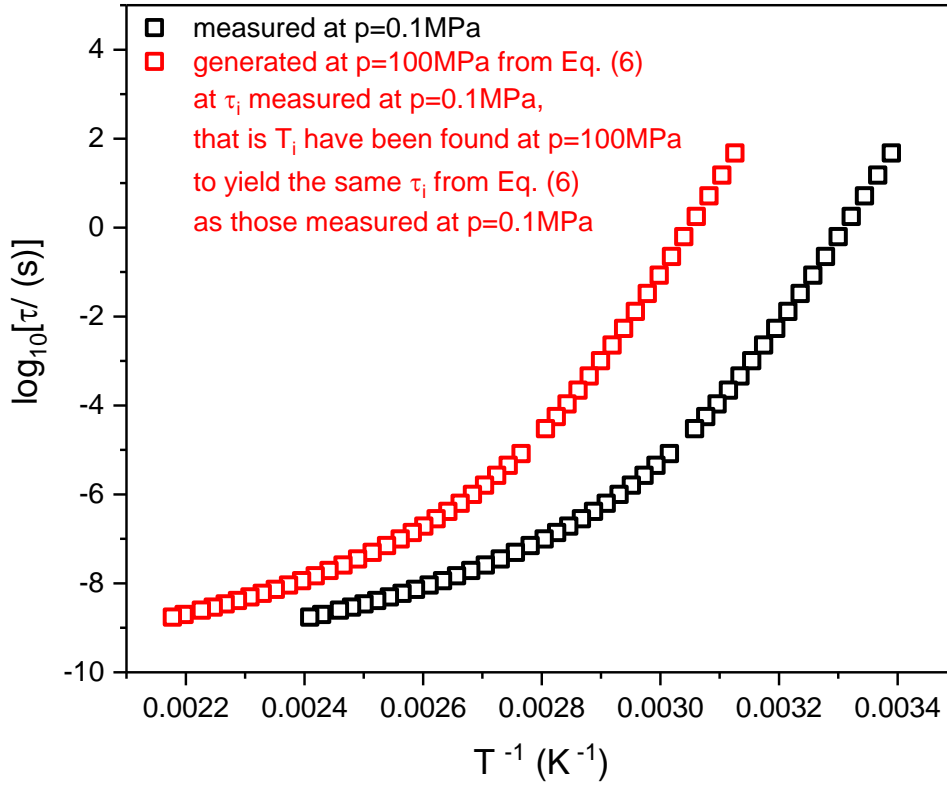


Fig. S5

The temperature dependences of the ambient pressure isobar of structural relaxation times determined from the dielectric measurements (open black squares) and the high pressure isobar of structural relaxation times generated from Eq. (6) at $p=100\text{MPa}$ (open red squares) at the same structural relaxation times as those established at ambient pressure.

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