

Pressure dependence of the glass temperature in supercooled liquids

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The description of the pressure evolution of the glass temperature $T_g(P)$ based on experimental data for diethyl phtalate is discussed. First, parameterizations of $T_g(P)$ experimental data applied are briefly given. Then a novel relation based on the modified Simon-Glatzel equation is proposed. Its applications may result in the appearance of the asymptotic temperature (θ) and the asymptotic pressure (π) previously postulated [E. Donth, *The Glass Transition: Relaxation Dynamics in Liquids and Disordered Materials*, Springer Series in Material Sci. II (Springer, Berlin, 1998), Vol. 48, pp. 6, 375]. The asymptotic pressure is hidden in the negative pressure domain. Such asymptotic behavior was absent for parameterizations of $T_g(P)$ data in glassy liquids applied up to now.

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INTRODUCTION

Despite the extensive studies on the glassy state, its nature remains puzzling. Hence, novel experimental results are of particular importance [1–21]. Most experimental research on the dynamics of supercooled liquids is based on temperature (T) measurements under atmospheric pressure [1,2] but vitrification occurs also as function of pressure (P) [1–21]. Both P and T paths lead to the structural arrest on the experimental time scale but their molecular picture is basically different. Slowing down of dynamics on cooling is related to the reduction of the kinetic energy while compression limits the free volume and consequently the rearrangement possibilities [1,2]. Pressure is also one of the most important parameters to control glass temperature (T_g) [1–21]. It is noteworthy that passing T_g is manifested in the scanning of some basic physical properties such as differential scanning calorimetry, viscosity or density [1], contrary to the set of fictive temperatures introduced by different physical models for glassy liquids [1,2]. The analysis of experimental data showed that dielectric relaxation time $\tau(T_g)=100$ s [2–21]. This constituted yet another practical way of T_g estimation, namely from the extrapolation of $\tau(T)$ dependence, usually parameterized via the Vogel-Fulcher-Tammann (VFT) relation. This method appeared to be a key tool for experimental determining of the pressure dependence of T_g , namely from broad band dielectric spectroscopy (BDS) studies [2–21]. Although high pressure tests on liquids have a long tradition ([22,23], and references therein) experiments enabling estimations of $T_g(P)$ dependence in glassy liquids did not start until the 1990s ([2–21], and references therein). Systematic exceeding of pressure $P=1$ GPa, necessary for testing any nonformal relations proposed for describing $T_g(P)$ dependence, has only been possible in recent years [4,9–12,16–20].

Experiments conducted up to now show an increase of $T_g(P)$ with rising pressure, in the form of a weakly bending down curve [4–21]. First attempts at parameterization of $T_g(P)$ experimental data used a power series, namely [3,5,6,8,9]

$$T_g(P) = T_g^0 + AP + BP^2, \quad (1)$$

where A and B are fitted parameters.

For pressures $P < 200$ MPa a linear term seems to deliver a fair description within experimental error [3]. The power series can be used for practical description and interpolation of experimental data but the lack of any physical background makes any extrapolation outside the experimental range unreliable. In 1999 Andersson and Andersson [4] postulated an empirical equation to parameterize $T_g(P)$ dependence in poly(propylene oxide) for the pressure range extended up to 1 GPa, namely,

$$T_g(P) = T_g^0 \left(1 + \frac{b}{a} P \right)^{1/b}. \quad (2)$$

In the following years relation (2) becomes a key tool for portraying the pressure evolution of the glass temperature in glass forming liquids [11–14,18–21]. It was shown in Refs. [10,12] that this dependence can be derived from the relation proposed by Avramov [7] for the comprehensive parameterization of the pressure and temperature evolution of viscosity or relaxation time, namely,

$$\log \tau = \log \tau_0 + 30 \log e \left(\frac{T_r}{T} \right)^{a'} \left(1 + \frac{P}{\Pi} \right)^{b'}. \quad (3)$$

Assuming $\tau(T_g)=100$ s and $T=T_g$ the above can be rearranged as follows [10,12]:

$$T_g(P) = T_r \left(\frac{A}{2 - \log \tau_0} \right)^{1/a'} \left(1 + \frac{P}{\Pi} \right)^{b'/a'}. \quad (4)$$

It is noteworthy that that coefficients a' and b' in relation (4) can be obtained from the comprehensive parameterization of $\tau(T, P)$ or $\eta(T, P)$ experimental data via relation (3) [10,12]. However, this assumes the knowledge of the fictive model temperature T_r , slightly different from T_g .

When discussing the pressure evolution of the glass temperature worth recalling is also the hypothesis that the pressure evolution of isochronal temperatures in supercooled liquids and polymers should follow a function with temperature (θ) and pressure asymptotes (π) asymptotes, common for dif-

ferent isochrones. For asymptotes $\theta > T_g + 100$ K and the negative pressure $\pi \approx -0.1$ GPa values were suggested [1,24]. It is noteworthy that relations (1)–(4) do not yield asymptotes and cannot be extended into the negative pressure domain.

This paper aims at discussing further origins of the Andersson and Andersson [4] formula (2). Additionally, the novel equation for portraying $T_g(P)$ experimental data, showing asymptotic temperature and pressure behavior postulated theoretically (see p. 5 and p. 375 in Ref. [1]) is given. The novel two-step way of analysis of $T_g(P)$ experimental data is also proposed. The first step is based on the derivative analysis of experimental data. It answers the question whether the proposed description can be applied and additionally reduces the number of fitted parameters. The discussion section is supported by the analysis of $T_g(P)$ experimental data in diethyl phtalate (DEP).

RESULTS AND DISCUSSION

When analyzing the pressure dependence of $T_g(P)$ it should be stressed that relation (2), has the form of the Simon-Glatzel (SG) relation [25] which for decades has been the basic tool for portraying the pressure evolution of the melting temperature of pure compounds [26–33]. Recalling the hypothesis of a hidden discontinuous or weakly discontinuous phase transition underlying the dynamic transformation near T_g [1] one may assume the validity of the Clausius-Clapeyron equation [34] for the gradient along the relevant phase transition line, namely,

$$\left(\frac{dP}{dT}\right)_{P_g, T_g} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \quad (5)$$

or

$$\left(\frac{dP}{d \ln T}\right)_{P_g, T_g} = \frac{\Delta H}{\Delta V}, \quad (6)$$

where ΔH is the latent heat and ΔV is the volume discontinuity related to the phase transition. It should be stressed that there is no clear evidence of the phase transition underlying the glass transformation and number of investigators wonder if a hypothetical phase transition is unreachable, avoided or simply nonexistent [1,2]. On the other hand pretransitional phenomena even well above T_g were reported in recent studies of magnitudes directly coupled to heterogeneities-fluctuations [35,36]. The underlying phase transition hypothesis seems to also support the universality (?) of the ratio between the glass temperature and the melting temperature $T_g/T_m \approx 2/3$, valid for organic liquids and molten oxides [1]. The Lindemann ratio rule, resulted from the Clausius-Clapeyron equation and characteristic for melting, was recently used for explaining the universal relaxation time $\tau(T_B) \approx 10^{-7}$ occurring at dynamic crossover above T_g [37].

Based on the discussion for the pressure evolution of the melting temperature [28] one can assume the linear dependence of the right-hand term on pressure,

$$T_g(P) \left(\frac{dP}{dT}\right)_{P_g, T_g} = \left(\frac{\Delta H}{\Delta V}\right)_{P_g, T_g} = b\Pi + b\Delta P, \quad (7)$$

where Π is the disposable pressure coefficient, $\Delta P = P - P_g^0$, P_g^0 is the reference glass pressure related to the reference glass temperature T_g^0 .

By integration, the relation of the same form as the SG equation [28] for the melting temperature is obtained, namely,

$$T_g(P) = T_g^0 \left(1 + \frac{\Delta P}{\Pi}\right)^{1/b}. \quad (8)$$

Noteworthy is the significant difference between relations (2) and (8). For relation (2) the prefactor $T_g^0 = T_g(P=0) \approx T_g(P=0.1 \text{ MPa})$. Determining the value of $T_g(P=0.1 \text{ MPa})$ is relatively simple, standard measurement under ambient pressure. This enables the reduction of fitted parameters. For relation (8), $T_g^0 = T_g(P_g^0)$ and consequently the fitting of $T_g(P)$ data can start from an arbitrary pressure. It is noteworthy that derivation of relations (8) via dependence (6) gives

$$\left(\frac{dP}{d \ln T}\right)_{P_g, T_g} = b\Pi + b\Delta P = (b\Pi - bP_g^0) + bP. \quad (9)$$

Consequently, the plot of the derivative of transformed experimental data namely, $(dP/d \ln T)_{P_g, T_g}$ vs P , should yield a linear dependence in the region of validity of relation (8). The slope of the straight line, analyzed via the linear regression, determines the power exponent b . Hence, the power coefficient in Eqs. (2) and (8) can be estimated before the final fitting, from the above derivative-based analysis.

It is well known that pressure always increases the glass temperature. However, in Ref. [1] the asymptotic behavior of $T_g(P)$ at extreme pressures was postulated. Relations (2) or (8) do not exhibit such behavior. But for the extreme pressures asymptote the condition $(T(P)/dP)_{P_g, T_g} \rightarrow 0$ takes place. This can be reached by the simply supplementation of relation (7), namely,

$$T_g(P) \left(\frac{dP}{dT}\right)_{P_g, T_g} = \left(\frac{\Delta H}{\Delta V}\right)_{P_g, T_g} = \frac{(b\Pi + b\Delta P)}{1 - c(b\Pi + b\Delta P)}. \quad (10)$$

By integrating this yields

$$T_g(P) = F(P)D(P) = T_g^0 \left(1 + \frac{\Delta P}{\Pi}\right)^{1/b} \exp\left(-\frac{\Delta P}{c}\right), \quad (11)$$

where $F(P)$ is the rising function and $D(P)$ is the damping function.

Analogous dependence was already successfully applied for portraying the pressure evolution of the melting temperature up to the extreme pressures region. Particularly, the possibility of reproducing the inflection of the melting temperature in this domain was shown [28–33].

The above analysis will be now applied to discuss the pressure evolution of the glass temperature in supercooled diethyl phtalate (DEP) presented in the inset in Fig. 1. Experimental results based on the estimation of BDS measure-

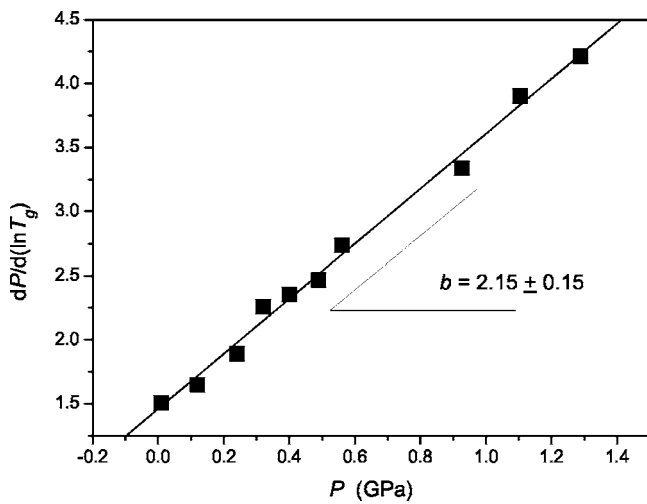


FIG. 1. Results of the derivative analysis of transformed experimental data from Fig. 1, based on relation (9). The slope of the straight line gives the power exponent in SG-based relations (2), (4), (8), and (11).

ments were taken from Ref. [16] (for $P=0.53, 0.93, 1.12,$ and 1.32 GPa) and have been supplemented by additional $T_g(P)$ data estimated from novel *BDS* measurements. These tests were carried out using the same experimental pressure set up as in Ref. [16].

Figure 1 shows behavior of $T_g(P)$ experimental data after derivative based transformation following relation (9), namely, $dP_g/d(\ln T_g)$ vs P_g plot. The obtained linear behavior shows the ability of the SG-based relations (2), (4), (8), and (11) for portraying $T_g(P)$ experimental data in DEP. This analysis also yielded the power exponent b which can be next used for the final fit of $T_g(P)$ via SG-based relation (8).

Figure 2 presents $T_g(P)$ experimental data and results of their parameterizations via relation (8) and the improved SG-based relation (11). Both relations are extended beyond the experimental range of pressures by fitting with the values of T_g^0 taken above and below the experimental range of data. For $T_g^0 < T_g(P=0)$ this yields values of P_g^0 located in the negative pressure domain. It is noteworthy that the SG-based relation (8) shows an asymptotic behavior in this domain.

This is clearly visible in Fig. 3 where the evolution of fitted parameters in relation (8) (P_g^0, Π) as a function of T_g^0 is presented. Noteworthy is a power-type decay on cooling of the disposable pressure coefficient $\Pi(T_g^0) = 1.95(T_g^0)^{-2.4}$ (kPa), clearly shown due to the log-log scale applied for the top and the right-hand axis in Fig. 3. The evolution of the reference glass transition pressure can be well portrayed by the first order exponential decay $P_g^0(T_g^0) = -0.63 + 0.036 \exp(T_g^0/64.1)$ (GPa), as shown by the solid curve related to the bottom and the left-hand axis in Fig. 3. The constant term in the latter relation determines the asymptotic negative pressure $\pi = -0.63$ GPa. When extended the SG-based relation (8) for higher temperatures it does not show any asymptotic as shown by the dashed curve in Fig. 1. However the extended SG-based relation (11), i.e., Eq. (8) supplemented by a damping term, exhibits a high temperature asymptote for $c = 2.38$ kPa. For smaller values of this

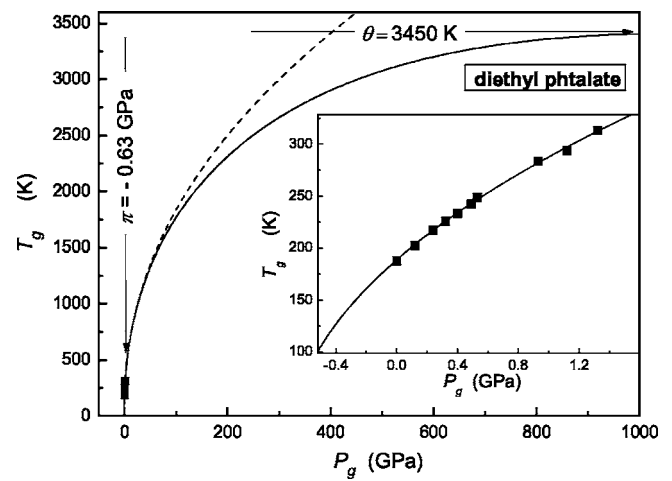


FIG. 2. The pressure dependence of the glass temperature in diethyl phthalate based on supplemented data from Ref. [16]. The dashed curve is parameterized via relation (9), namely $T_g(P) = 10.5[1 + (P - 0.625)/0.00097]^{1/2.15}$. The solid curve is described by relation (11): $T_g(P) = 10.3[1 + (P - 0.625)/0.001]^{1/2.15} \exp[-(P - 0.625)/0.00042]$. Asymptotic pressure ($-\Pi$) and temperature (θ) are shown in the figure.

coefficient the damping is too weak and the increase of pressure permanently increases the glass temperature. For $c < 2.38$ kPa the inflection of $T_g(P)$ dependence for extreme pressures occurs. It is noteworthy that for $P_g < 20$ GPa both the SG-based nondamped relation (8) and the extended SG-based damped relation (11) coincides within the experimental error possible in practice. Relation (11) supported by the analysis discussed above yields $\theta = 3450$ K and $\pi = -0.63$ GPa asymptotes of the pressure dependence of the glass transition in DEP.

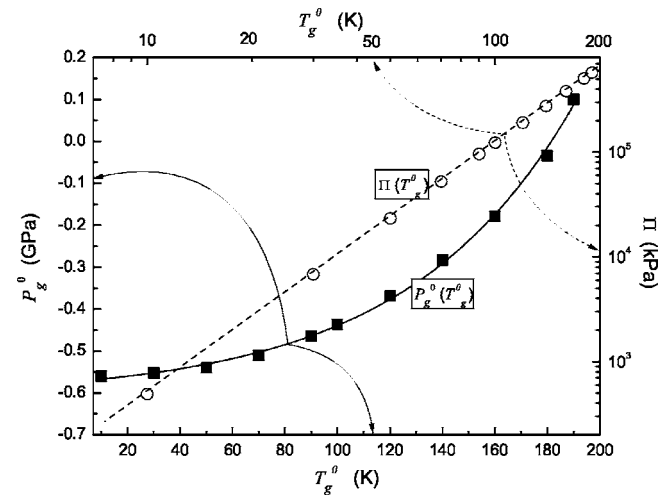


FIG. 3. The evolution of fitted parameters in SG-based relation (8) as a function of the reference temperature T_g^0 . The solid curve is portrayed by $P_g^0(T_g^0) = -0.63 + 0.036 \exp(T_g^0/64.1)$ (GPa). It is related to the left-hand (P_g^0) and the bottom (T_g^0) axis. The log-log scale of the right-hand axis (Π) and the top axis (T_g^0) shows the validity of the power dependence $\Pi(T_g^0) = 1.95(T_g^0)^{-2.4}$ (kPa) (dashed line). Arrows indicate axis related to the given dependence.

Over the last decade it was clearly showed that positive pressure states can be smoothly extended into the metastable negative pressure domain, with no singularity at $P=0$ [38,39]. Worth recalling are results in critical blends [39,41] and in water [39,42] which showed that the deriving of ultimate equations of state is possible provided the positive and negative domains are included [38,40]. Any liquid can be stretched only down to liquid-gas spinodal where the liquid breaks and homogeneous nucleation occurs. However, negative pressure experiments are extremely difficult due to heterogeneous nucleation, changing a liquid back into the positive, equilibrium, domain before reaching the spinodal [38–42]. Perfect degassing, lack of impurities and control of disturbances from experimental conditions are basically important for approaching the “breaking liquid” spinodal hidden in the naturally metastable negative pressure domain [39]. Moreover, the position of the spinodal is strongly temperature depend [38,39]. For instance for water values ranging from -0.5 MPa to -150 MPa can be found [39,42]. The latter value is probably the lowest negative pressure value reached for a liquid up to now. No direct experimental studies giving the evolutions of dynamic properties or characteristic temperatures in the negative pressure domain in glassy liquids are available yet. However, recently Lach *et al.* [43] carried out dynamic yield stress experiment for few polymeric glass formers near T_g . Considering the yield stress as the equivalent of the negative pressure breaking limits ranging from -0.015 GPa to -0.128 GPa were obtained. These values are smaller than $\pi \approx -0.63$ GPa reported in this paper for DEP. However, the latter value may be considered only as the estimation of the lowest possible negative pressure

possible to approach for low temperatures. For higher temperatures the position of spinodal $\pi(T)$ should be expected for less negative pressures. Moreover, available results for liquids shows that only a sequence of experiments can yield a proper estimation of the spinodal position due the parasitic factors mentioned above.

Concluding, the description of the pressure evolution of the glass temperature was discussed. Particularly, the possible significance of the modified Simon-Glatzel-type equation was indicated. The proposed novel equation of portraying $T_g(P)$ data may result in the appearance of the asymptotic temperature and the asymptotic pressure, postulated in [1], pp. 6 and p. 375. The postulated in this reference typical asymptotic value $\pi \approx -0.1$ GPa differ from the obtained $\pi \approx -0.63$ GPa but order of magnitude is in agreement. In this respect it is noteworthy that for higher temperatures the “breaking liquid” spinodal location $\pi(T)$ may be expected for much less negative.

Near asymptotes relaxation time isochrones approach one another. Hence, the estimation of θ and π asymptotes may facilitate the obtaining of a glass close to the “ideal glass” in the future. However, this only seems possible in the negative pressure domain.

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