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Effect of high pressure on the relaxation dynamics of glass-forming liquids

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Abstract

A glass is usually formed by cooling a liquid at a rate sufficient to avoid crystallization. In the vicinity of the glass transition the structural relaxation time increases with lowering temperature in a non-Arrhenius fashion and the structural relaxation function reveals a non-Debye behaviour. However, liquid can be also vitrified by keeping it at a constant temperature and increasing the pressure. This pressure-induced transition to the glassy state is also accompanied by dramatic changes in the relaxation dynamics. Herein we discuss the behaviour of the structural relaxation times of glass-forming liquids and polymer melts under high pressure.

1. Introduction

A commonly used and most convenient method for producing glass from liquid consists in cooling liquid at a rate sufficient to avoid crystallization. During the liquid–glass transition many physical properties of materials, e.g. specific heat, specific volume, Young's modulus, dielectric permittivity, dielectric relaxation time, and viscosity, as well as coefficients of volume expansion, compressibility, diffusion, and refractive index, change in some characteristic ways [1, 2]. One of the most intriguing features of the glass-formation phenomenon is a dramatic change in molecular dynamics. A very useful method for the investigation of molecular dynamics near the glass transition is dielectric relaxation spectroscopy [3]. On approaching the glassy state, the dielectric structural α -relaxation time τ_α of a liquid rapidly increases by many orders of magnitude in a narrow temperature range. This significant feature of molecular dynamics related to the vitrification process is characterized by the non-Arrhenius temperature dependence of τ_α . Such a non-Arrhenius behaviour is universal, because it can be observed in different classes of material, e.g. van der Waals liquids, polymers, and hydrogen-bonded systems. In the vicinity of the glass transition temperature T_g the dependence $\tau_\alpha(T)$ is often described by means of the Vogel–Fulcher–Tamman (VFT) law [4],

$$\log \tau_\alpha = \log \tau_\infty + \frac{D_P T_0}{T - T_0}, \quad (1)$$

where τ_∞ is the fast relaxation time limit approached at ‘infinitely’ high temperature, D_P is a material constant, and T_0 indicates the temperature where the relaxation time is expected to diverge. A traditional measure of the non-Arrhenius behaviour of the isobaric dependence $\tau_\alpha(T)$ is fragility. There are various definitions of this parameter [5–7], but from among them the most common way of quantifying the isobaric fragility is a steepness index,

$$m_P = \left. \frac{d \log \tau_\alpha}{d(T_g/T)} \right|_{T=T_g}. \quad (2)$$

According to this definition, the fragility means the activation energy $E_P(T_g)$ at constant pressure P divided by the glass transition temperature, i.e. $m_P = E_P(T_g)/RT_g$, where R is the gas constant. The fragility m_P is a material-dependent parameter. Angell [7, 8] has proposed a classification of materials into fragile, intermediate, and strong liquids. The fragile materials, which have large values of m_P , exhibit a significant deviation from the Arrhenius behaviour of $\tau_\alpha(T)$, in contrast to strong materials.

Besides the thermal way of forming a glass from a liquid there is another method for vitrifying, which consists in keeping the liquid at a constant temperature and increasing the pressure [9]. Compression considerably influences intermolecular distances; consequently, the α -relaxation can be considered mainly as a volume-activated process. Then, according to the Arrhenius law the α -relaxation time can be expressed by using the work required to be done by a molecule for its reorientation instead of the thermal activation energy,

$$\log \tau_\alpha = \log \tau_0 + \log(e) \frac{P \Delta V^\#}{RT}, \quad (3)$$

where $\Delta V^\#$ is an activation volume and τ_0 is the value of τ_α at atmospheric pressure. The activation volume mirrors the volume requirement for local motion. In accordance with transition state theory [10], $\Delta V^\#$ is defined as the difference between the volumes occupied by a molecule in activated and non-activated states. The pressure dependence of τ_α can be satisfactorily described by equation (3), usually in a very narrow pressure range. There is much experimental evidence [11–13] that the pressure-induced vitrification at constant temperature is related to a dramatic slowing down in the molecular dynamics. Then, the isothermal dependences $\log \tau_\alpha(P)$ are nonlinear, similarly to the above-mentioned isobaric dependences $\log \tau_\alpha(T^{-1})$. Therefore, the activation volume has to be a function of P and T . The values of $\Delta V^\#$ can be determined by using the following formula:

$$\Delta V^\# = RT \ln(10) \left(\frac{\partial \log \tau_\alpha}{\partial P} \right)_T. \quad (4)$$

In order to describe the nonlinear isothermal dependences $\log \tau_\alpha(P)$ one often uses the pressure-dependent VFT formula proposed in [14] and [15]:

$$\log \tau_\alpha = \log \tau_0 + \log(e) \frac{D_T P}{P_0 - P}, \quad (5)$$

which can be derived by replacing T^{-1} by P in equation (1). It is worth noting that the pre-exponential factor τ_0 is the relaxation time at ambient pressure. D_T is the so-called ‘strength’ parameter and P_0 is the pressure at which τ_α diverges.

Considering the influence of pressure on dielectric relaxation processes, one should not forget a general experimental fact recently discovered in glass-formers. The dispersion of structural relaxation is constant for a given material at a fixed value of τ_α and is independent of thermodynamic conditions (T and P), i.e. the shape of the α -relaxation peak depends only on the relaxation time [16].

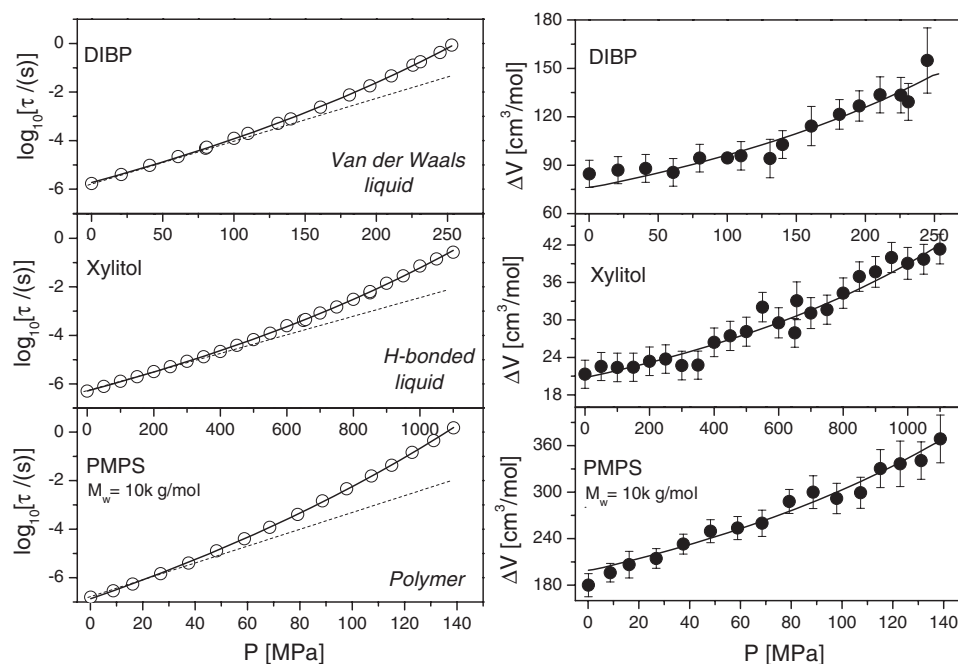


Figure 1. The left panel shows the pressure dependences of isothermal α -relaxation times for three kinds of material: di-isobutylphthalate (DIBP) [12], xylitol [18], and polymethylphenylsiloxane (PMPS) of molecular weight of 10000 g mol^{-1} [19] represent van der Waals liquids, H-bonded systems, and polymers, respectively. Solid lines are fits of the experimental data to equation (5). Dashed lines demonstrate how the pressure dependences would look in the case of simply volume-activated processes which should obey the Arrhenius law with $\Delta V^\ddagger = \text{const}$. Pressure dependences of the activation volume calculated from the definition (equation (4)) for DIBP, xylitol and PMPS are presented in the right panel.

Studying the effect of pressure on molecular dynamics, one feels a need to find a parameter which could classify glass-forming liquids in accordance with their differences in pressure dependence of the structural relaxation times. By analogy to isobaric fragility, one can define the isothermal fragility which can be used to compare the pressure dependences of τ_α for various materials. In this work we analyse the pressure dependence of structural relaxation times of various glass-forming liquids and polymers using the activation volume and the isothermal fragility concepts. Moreover, we also study the effects of temperature on the isothermal fragility and pressure on the isobaric fragility. Finally, we show a new way of scaling for isothermal α -relaxation times, and its relation with the thermodynamical scaling [17].

2. Pressure effect on ΔV^\ddagger and m_P

In principle, pressure and temperature are equivalent thermodynamic parameters, but they affect molecular systems in a different way. Temperature mainly influences the rotational and vibrational excitation of molecules, whereas pressure changes intermolecular distances. In the case of isothermal measurements, an especially important activated parameter is the activation volume, which can be defined on the basis of the dependences of α -relaxation times versus P and T (equation (4)). According to the definition of ΔV^\ddagger , the nonlinear increase of isothermal $\log \tau_\alpha$ with pressure causes the activation volume to increase with P . It seems that this pattern

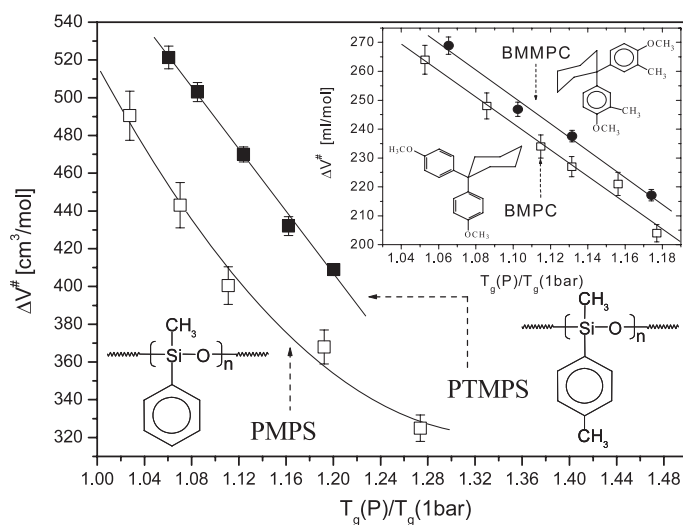


Figure 2. Temperature dependences of the activation volume calculated from equation (6) for different isobars at constant α -relaxation time for the polymers PTMPS and PMPS [20]. Analogous dependences are shown in the inset for the van der Waals liquids BMMPC and BMPC [21].

of behaviour has universal character because it can be observed for different kinds of material, such as van der Waals liquids and polymers, and also hydrogen-bonded systems (figure 1).

As can be seen in the right panel of figure 1, the values of $\Delta V^\#$ also increase in some nonlinear way. This reflects the strong influence of density changes caused by compression on investigated molecular reorientations. The value of the activation volume $\Delta V^\#$ provides valuable information on the pressure sensitivity of the structural relaxation times. One can see in the right panel of figure 1 that polymer PMPS has to have considerably larger $\Delta V^\#$ to reorient than is necessary for small molecules (DIBP and xylitol). In fact, the structural relaxation slows down by about six decades of τ_α in the 140 MPa range for PMPS, whereas DIBP and xylitol require the increase of pressure by 250 and 1100 MPa respectively in order to achieve the same slowing down in the dynamics.

As we have already demonstrated, the activation volume usually increases with pressure. Now it is interesting to analyse the behaviour of $\Delta V^\#$ as a function of temperature at constant α -relaxation time. Such a behaviour is shown in figure 2 for polymers (PMPS, PTMPS) as well as van der Waals liquids (BMPC, BMMPC). In this case $\Delta V^\#$ is plotted as a function $T_g(P)/T_g(1\text{ bar})$ at one constant τ_α . It is worth noting that at a given $T_g(P)/T_g(1\text{ bar})$ the activation volume is larger for PTMPS than it is for PMPS. PTMPS in comparison to PMPS has an additional methyl group attached to the phenyl ring. Thus, the molecular volume of the repeating unit of PTMPS is larger than it is for PMPS. A similar pattern of behaviour can be observed for BMMPC and BMPC. The former molecule has two additional methyl groups. Therefore, one can claim that $\Delta V^\#$ reflects the molecular size of the relaxing units. Thus, larger molecules need more space to reorient than smaller ones. This regularity can also be nicely demonstrated for a polyalcohol series. Calculating $\Delta V^\#$ from the following expression [22],

$$\Delta V^\# = \ln(10) R m_P \frac{dT_g}{dP}, \quad (6)$$

which relates the activation volume to the isobaric steepness index, one obtains that $\Delta V^\#$ increases as the molecular weight M_w of the studied polyalcohols increases (see figure 3).

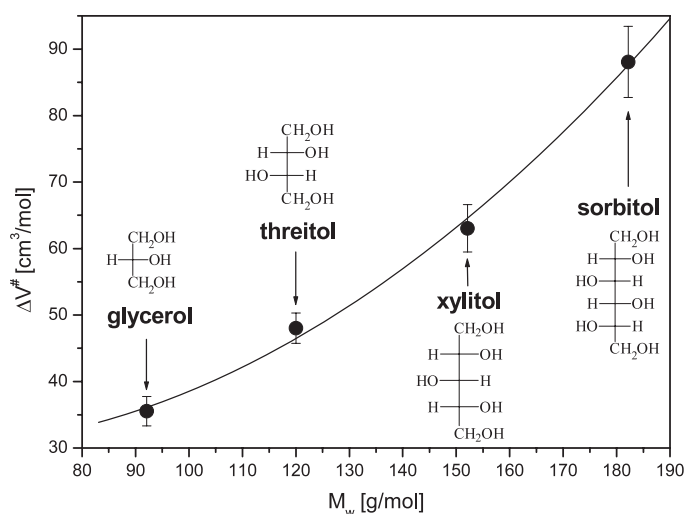


Figure 3. Plot of the activation volume for a polyalcohol series versus the molecular weight of these compounds. The values $\Delta V^\#$ are calculated from equation (6) with the values of dT_g/dP and m_p collected in table 1.

Table 1. The isobaric fragility, m_p , the glass transition temperature, T_g , and the value of the pressure derivative, dT_g/dP , at atmospheric pressure for a polyalcohol series.

Polyalcohol	dT_g/dP (K GPa ⁻¹)	m_p	T_g (at $\tau = 100$ s) (K)
Glycerol	35 ± 3	57	188.4
Threitol	33 ± 5	79	224
Xylitol	34 ± 2	94	247
Sorbitol	40 ± 5	128	267

It is interesting that the values of the derivative dT_g/dP are nearly the same for all these compounds. Therefore, the increase of $\Delta V^\#$ is mainly related to the increase of the isobaric fragility m_p with M_w of the analysed polyalcohols (see table 1).

As shown above, the activation volume is pressure dependent. Therefore, according to the relation given by equation (6) it can be expected that the isobaric fragility m_p also depends on P . Experimental data confirm that the isobaric steepness index usually decreases with increasing pressure [23–25]. As can be seen in figure 4, this pattern of behaviour is commonly observed for van der Waals liquids (PDE and BMMPC).

So far, we know only one exception from this rule. This van der Waals material is DHIQ, whose isobaric fragility seems to increase with compression [27]. Very complex behaviour of m_p is found in the case of some H-bonded systems. Casalini and Roland [28] analysed the pressure dependence of the fragility for propylene glycol oligomers. As an example, the isobaric fragility for dipropylene glycol (DPG) increases with pressure (see figure 4). Such a behaviour is usually ascribed to a decrease of hydrogen bonding. This is because higher pressure corresponds to higher temperature, and consequently leads to the loss of hydrogen bonds. To test if the pressure dependence of m_p has some asymptotic character we measured an additional isobar at 1.7 GPa for DPG. It turned out that m_p drops at this extremely high pressure (see figure 4). This means that above some characteristic value of pressure this H-bonded system behaves as a normal van der Waals liquid.

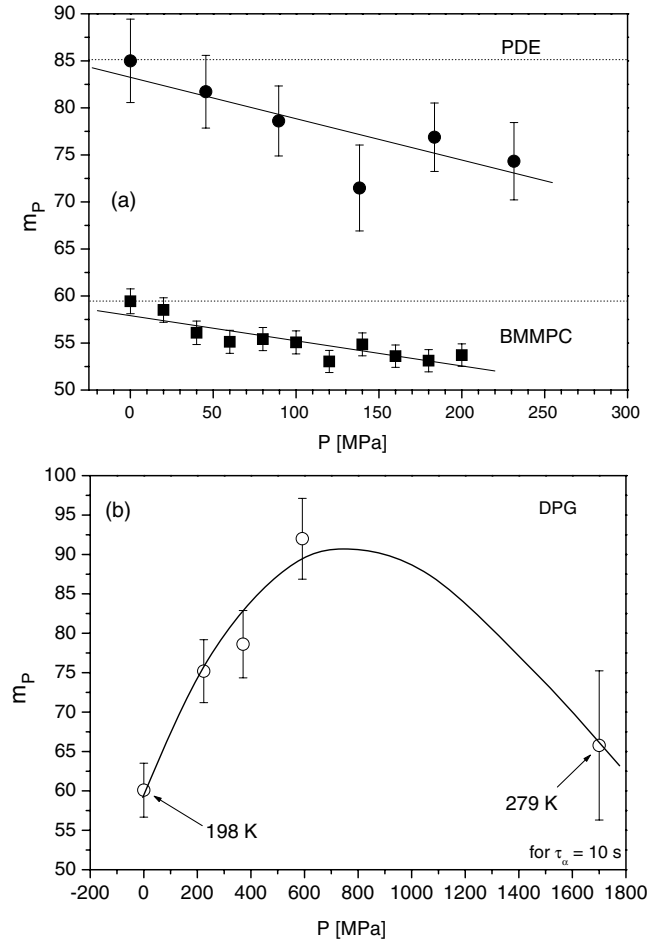


Figure 4. Pressure dependences of the isobaric fragility for (a) van der Waals liquids PDE [23] and BMMPC [24], and (b) DPG [26] belonging to H-bonded systems.

3. Isothermal fragility

Similarly to the fragility parameter at constant pressure, m_P defined by equation (2), one can construct the fragility parameter at constant temperature as the isothermal steepness index

$$m_T = \left. \frac{d \log \tau}{d(P/P_g)} \right|_{P=P_g}, \quad (7)$$

which can be used for characterizing the pressure dependences of the structural relaxation times of various materials. From the above definition and equation (3) it results that the isothermal fragility is the ratio of the work done by a molecule to move or jump to another site at the glass transition pressure P_g divided by the glass transition temperature T_g , i.e. $m_T = P_g \Delta V^\#(P_g) / RT_g$. An ideal strong liquid subjected to isothermal compression is characterized by the pressure-independent activated volume. Its isothermal steepness index $m_T = \log \tau_\alpha(T, P_g) - \log \tau_0(T, P = 1 \text{ bar})$ as it results from the proposed interpretation of m_T and equation (3). A convenient way to compare the pressure dependences of τ_α consists in drawing a plot $\log \tau_\alpha(P/P_g)$ that is analogous to the temperature scaling plot

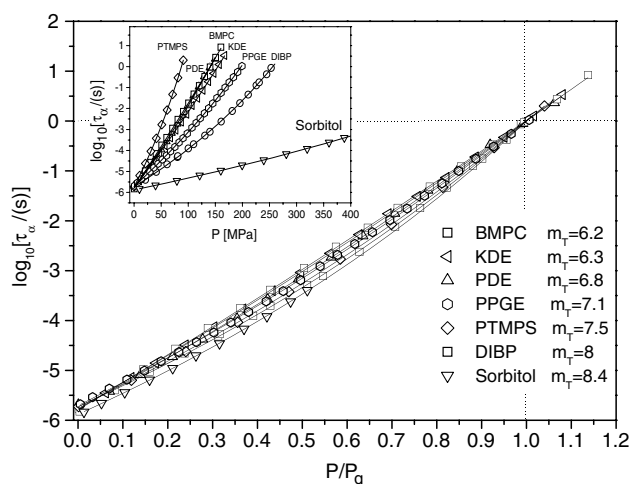


Figure 5. The pressure scaling plot for several glass-forming liquids. The inset shows the isothermal pressure dependences of the structural relaxation times with the same τ_α at $P = 1$ bar, which are used to perform the scaling plot. The solid lines are fits of the experimental data to equation (5).

$\log \tau_\alpha(T_g/T)$ [13]. Unfortunately, there are some inconveniences in the introduced definition of m_T , caused by the fact that $\log \tau_0$ depends on T , and consequently m_T changes with T . At first, in order to construct the pressure scaling plot for different materials one should take isotherms with the same relaxation times at ambient pressure. Such isothermal dependences $\log \tau_\alpha(P/P_g)$ for several glass-forming liquids and their pressure scaling plot are shown in figure 5. This scaling plot allows us to qualitatively compare materials in respect of the degree of deviation from the Arrhenius behaviour which characterizes simply activated processes with $\Delta V^\ddagger = \text{const}$. The new definition of the steepness index (equation (7)) enables us to quantify this deviation. From among the analysed materials (see figure 5) one can establish that sorbitol is the most fragile liquid ($m_T = 8.4$), whereas BMPC can be classified as the strongest one ($m_T = 6.2$).

The second problem is that drawing the analogue of the temperature scaling plot does not make any sense, if we want to compare the curvatures of isotherms for one material. In that case, as can be seen in figure 6(a), m_T always decreases with decreasing T due to the increase of $\log \tau_\alpha$ at ambient pressure with decreasing T . To avoid this problem one can analyse a volume scaling plot $\log \tau_\alpha(V_g/V)$ instead of $\log \tau_\alpha(P/P_g)$. In this context, pressure and volume are equivalent thermodynamic parameters, because the change of P leads only to a change of V when $T = \text{const}$. Then, all isotherms for one material fall onto one master curve, as is shown in figure 6(b) for PTMPS.

4. New look at thermodynamical scaling

The concept of thermodynamic scaling of structural relaxation times of supercooled liquids has recently been studied by several groups [17, 29–35]. Casalini and Roland [31] have shown that α -relaxation times measured at different T and P can be collapsed onto one master curve by plotting τ_α as a function of $\Gamma = T^{-1}V^{-\gamma}$. The scaling exponent γ is the material constant, which does not depend on the thermodynamic variables P , V and T . Similar scaling behaviour is also observed for isothermal α -relaxation times plotted versus V_g/V . It is shown, for instance, in the case of PDE in figures 7(a) and (b). Both the Γ and V_g/V scalings have

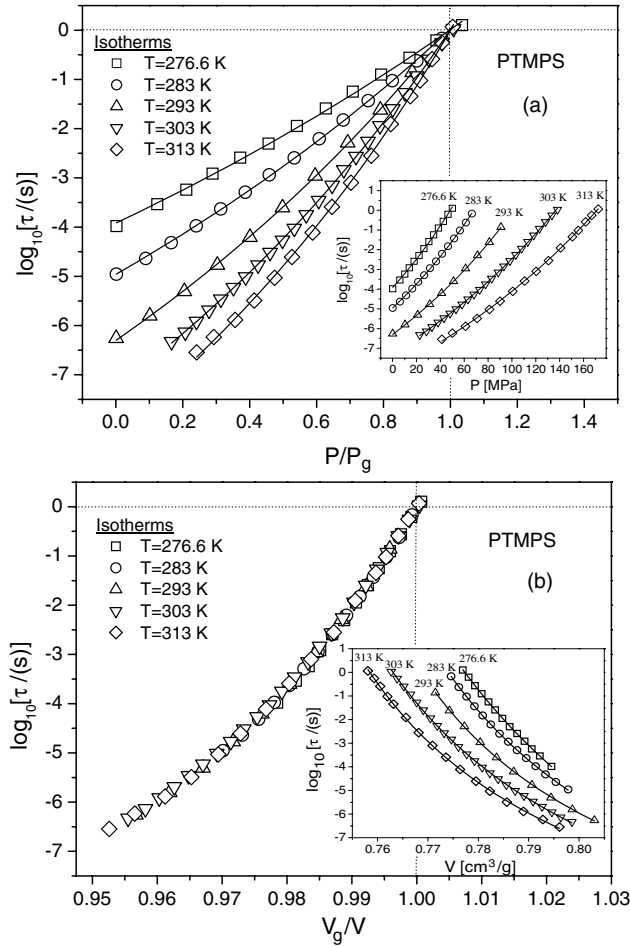


Figure 6. Isothermal dependences of structural relaxation times for PTMPS: (a) the pressure scaling plot constructed by means of the pressure dependences of α -relaxation times at several temperatures depicted in the inset. The solid lines are fits of the experimental data to equation (5); (b) the volume scaling plot drawn by using the volume dependences of α -relaxation times at several temperatures shown in the inset.

quite universal character because they are satisfied for polymers (figure 6(b)) as well as van der Waals liquids (see figures 7(a) and (b)).

However, the two kinds of scaling considered do not work for some H-bonded liquids. As an illustration of these problems we show in figures 8(a) and (b) that dielectric data for DPG cannot be scaled. The fact that there is no scaling of the relaxation data for H-bonded systems is due to high sensitivity of such materials to changing P and T , because the thermodynamic conditions strongly affect the degree of H-bonds.

It is worth finding a relation between these two kinds of scaling. In order to do that, one rewrites the quantity Γ in the following form:

$$T^{-1}V^{-\gamma} = \left(\frac{V_g}{V}\right)^{\gamma} T^{-1}V_g^{-\gamma}. \quad (8)$$

If the Γ scaling is satisfied the exponent γ is constant and at $T = T_g$ one can formulate the

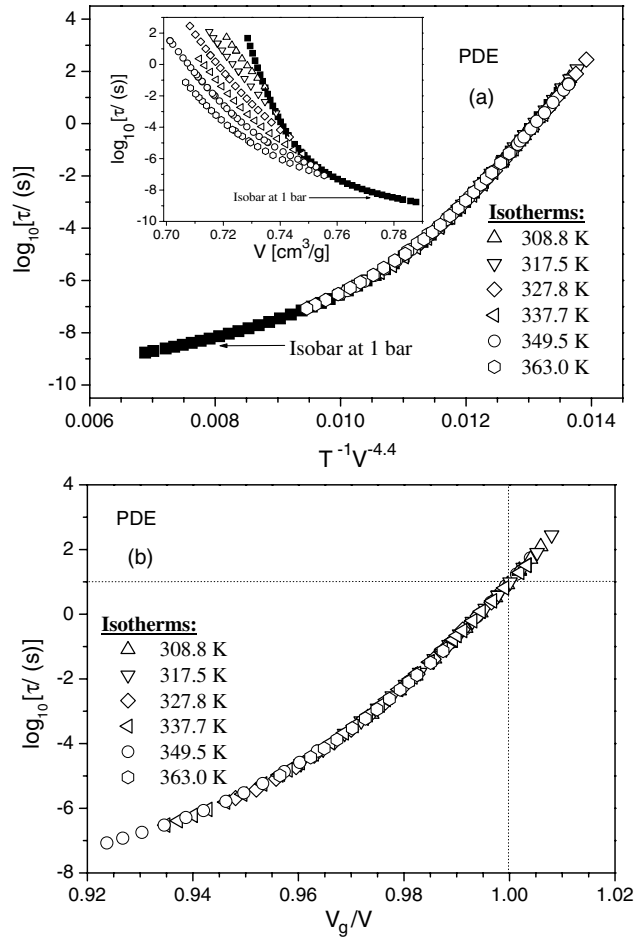


Figure 7. Scaling of structural relaxation times for PDE: (a) the thermodynamical scaling versus the quantity $\Gamma = T^{-1}V^{-\gamma}$. The inset shows the isotherms and atmospheric isobar used as functions of volume; (b) the scaling plot of those isotherms versus V_g/V .

condition

$$T_g^{-1}V_g^{-\gamma} = \text{const.} \tag{9}$$

From equations (8) and (9) it can be concluded that the ratio V_g/V itself leads to the scaling of isothermal relaxation times.

The condition equation (9) enables us to find a convenient method for determining the scaling exponent γ . From equation (9) there results the linear dependence $\log T_g(\log V_g)$,

$$\log T_g = A - \gamma \log V_g \tag{10}$$

whose parameters A and the scaling exponent γ can be obtained by simple linear regression. Plotting $\log T_g$ versus $\log V_g$ for PDE (see figure 9) and using equation (10), we find for dielectric data that the exponent γ is equal to 4.4, which corresponds to its value obtained from the standard procedure of thermodynamical scaling.

Another way of determining values of T_g and V_g can be by performing *PVT* measurements. It is interesting to see in figure 9 that the dependence $\log T_g(\log V_g)$ derived

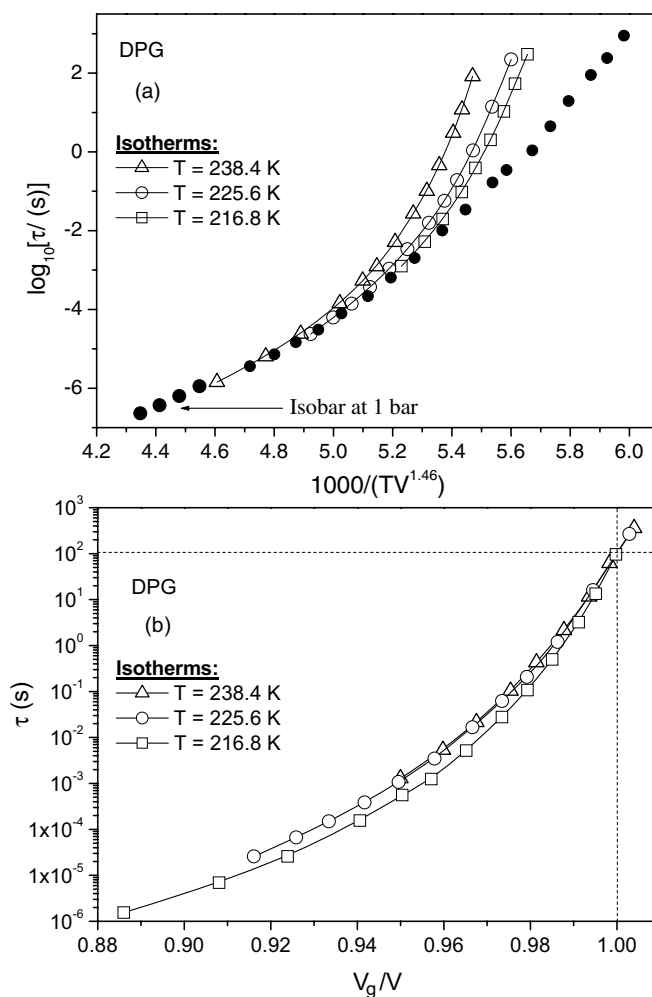


Figure 8. No scaling of structural relaxation times for DPG: (a) plot of α -relaxation times versus the quantity $\Gamma = T^{-1}V^{-\gamma}$ [36]; (b) the scaling plot of isothermal α -relaxation times versus V_g/V .

from PVT measurements (shown in the inset in figure 9) has the same slope γ as that found for dielectric data. This means that the dynamic and thermodynamic properties are expected to be strongly correlated.

5. Summary

There are generally two ways of vitrification, i.e. isobaric cooling and isothermal compression. In order to characterize the molecular dynamics related to these different methods of glass formation we need to find some parameters, and their dependences on thermodynamical variables. One of the most important values describing the dynamic behaviour of supercooled liquids is the fragility. On the basis of this parameter, glass-forming liquids can be classified into two classes, strong and fragile, depending on the form of the experimental functions $\log \tau_\alpha(T_g/T)$ and $\log \tau_\alpha(P/P_g)$, by means of the isobaric fragility m_P and the

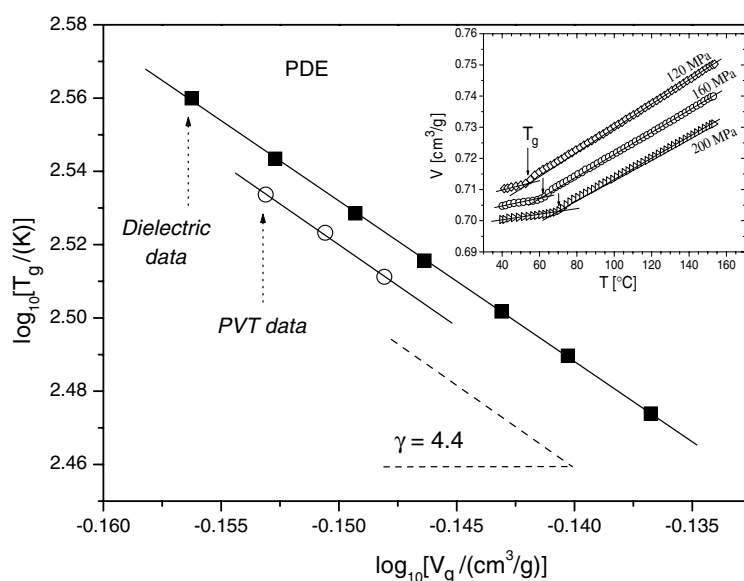


Figure 9. Logarithmic plot of the glass transition temperature T_g versus the glass transition volume V_g for PDE. Closed squares indicate data from dielectric measurements. Open circles represent data from PVT measurements. Solid lines are fits of those data to equation (10) with the same slope γ , which means the thermodynamical scaling exponent. The inset shows a plot of volume versus temperature obtained from PVT measurements near the glass transition, which enabled us to find the points (T_g, V_g) used for determining the scaling exponent γ from PVT measurements.

isothermal fragility m_T , respectively. However, the definition of the isothermal fragility has a disadvantage, which consists in the dependence of m_T on the structural relaxation time at atmospheric pressure. Therefore, the scaling plot of the dependences $\log \tau_\alpha(P/P_g)$ requires isotherms with the same relaxation time at ambient pressure for comparing various materials in terms of their isothermal steepness index. We proposed to solve this problem by drawing the scaling plot of the dependences $\log \tau_\alpha$ versus V_g/V instead of $\log \tau_\alpha(P/P_g)$. In this way we found that for non-associated liquids the experimental functions $\log \tau_\alpha(V_g/V)$ can be successfully grouped onto one master curve for all measured temperatures.

Isobaric and isothermal dielectric measurements provide some interesting information about the effect of the thermodynamical variable on parameters characterizing the molecular dynamics of the vitrification process. The influence of pressure on the growth of the activation volume seems to be universal, because this pattern of behaviour can be observed for various kinds of glass-forming liquid. The magnitude of ΔV^\ddagger is the same order as the molecular size or repeating unit in the case of polymers. The isobaric fragility m_p usually decreases with increasing P for van der Waals materials and polymers, whereas the dependence $m_p(P)$ for H-bonded systems is more complex due to the strong effect of thermodynamical conditions on the degree of H-bonds. It is evident that structural relaxation times for van der Waals liquids and polymers expressed in terms of V_g/V can be superimposed. Consequently, the isothermal steepness index is temperature independent for these materials. In contrast, the V_g/V scaling is not observed for H-bonded liquid.

Both the thermodynamical scaling versus the quantity $\Gamma = T^{-1}V^{-\gamma}$ and the scaling in terms of V_g/V well work for van der Waals and polymer materials, whereas these methods are not sufficient to scale the relaxation times for H-bonded systems. Similar behaviour of the

considered kinds of scaling is quite natural because the procedure using V_g/V results from the thermodynamical scaling for isothermal processes.

Finally, the exponent γ for the Γ scaling can be easily determined from linear regression of the experimental dependence $\log T_g(\log V_g)$. Using this method one can obtain the same value of γ from both dielectric and PVT measurements. The result implies the existence of strong correlations between dynamic and thermodynamic properties.

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