

Scaling of high-pressure viscosity data in low-molecular-weight glass-forming liquids

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We discuss the phenomenology related to the pressure behavior of viscosity in low-molecular-weight glass-forming liquids. We show that the effect of pressure on viscosity in two examined glass-forming systems, salol and ortho-terphenyl, can be satisfactorily described, over considerable ranges of pressure (up to 1 GPa) and temperature (300–425 K), by the two-parameter pressure law which has been proposed previously for the relaxation time shift. The presented analysis indicates that one of the parameters (the pressure counterpart of the Vogel-Fulcher-Tammann law parameter D , which accounts for the fragility of a glass former) is independent of temperature in salol and ortho-terphenyl. As a consequence, the scaling plot which normalizes data collected for different temperatures can be constructed for a given glass former. On the basis of the presented considerations, a general form of the temperature-pressure viscosity “equation of state” is proposed. [S0163-1829(99)14329-7]

I. INTRODUCTION

The most directly noticeable thing that can be observed when a liquid is cooled towards its apparent glass transition temperature T_g is the enormous increase of its viscosity. This phenomenon is normally studied by measuring the viscosity as a function of temperature. It is, however, well known that, alternatively to cooling, the glass transition can be achieved by squeezing. Studies of the effect of pressure on viscosity are rare due to the considerable experimental difficulties which are involved. Temperature and pressure are generally treated as equivalent thermodynamic variables, but the effects they exert on vitrification processes may be different. While temperature mainly influences processes associated with the activation energy (such as excitation of rotational energy states), pressure leads to changes in intermolecular distances. Therefore viscosity measurements carried out during isothermal compression^{1–3} can deepen our understanding of the glassy state, providing complementary information to those acquired from isobaric temperature-dependent data. An important question—whether it is temperature or density (or comparable contribution from both) which plays the role of the dominant thermodynamic variable governing the underlying physical processes in the glassy state—has been recently followed by several authors.⁴

During recent years, progress in the studies of glass-forming systems was stimulated by the development of the rolling ball viscometry in a diamond anvil cell, which has allowed the measurement of viscosity over a wide range of pressure (up to a few GPa).^{1–3} The major problem related to this kind of study is that although the viscosity can be measured under extremely high pressure, its behavior in the vicinity of the glass transition cannot be directly studied. Extrapolation of experimental data over a wide range of viscosity is often required for this effect. The first experimental results collected using the above technique provided an assessment of the free volume theory. The subsequent papers, however, reported much less agreement of the free volume expression with experimental findings. Most recently, Schug and co-workers³ have reported measurements

of the viscosity of ortho-terphenyl and salol under pressure, pointing out that the free volume expression fails to satisfactorily fit these data. To sum up, despite the growing amount of collected experimental results, a satisfactory description of the observed pressure viscosity behavior is still not established. The relationship which accounts for the latter would be crucial not only from a scientific point of view, but it would also be of importance as regards some applications, with lubrication technology being one of them.

In a number of recent papers,^{5–8} two of us have demonstrated on the basis of high-pressure isothermal measurements that the dielectric relaxation time pressure characteristics of several different fragile glass-forming liquids follows the phenomenological expression

$$\log_{10}\tau = \log_{10}\tau_0 + \frac{C_p P}{P_0 - P}, \quad (1)$$

where $\log_{10}\tau_0$ is the relaxation time measured under atmospheric pressure, P_0 is the pressure of the ideal glass transition, and C_p is a dimensionless factor defined analogously to the parameter D which occurs in the temperature Vogel-Fulcher-Tammann (VFT) law⁹ and which accounts for the fragility of a given glass-former. Interestingly enough, two regimes can be distinguished in Eq. (1): the Arrhenius regime at $P \ll P_0$ and the non-Arrhenius one at higher pressures.⁸

In the present paper we apply the above relationship to the pressure behavior of viscosity in glass-forming liquids and reanalyze the experimental results for ortho-terphenyl and salol, which have been obtained by Schug and co-workers.³ The above analysis reveals features of the temperature dependence of the parameters which account for the fragility of glass formers and the pressure of the ideal glass transition. The considerations presented lead also to some indication as to the general form of the relationship which accounts for the combined temperature-pressure dependence of viscosity in glass-forming liquids.

II. RESULTS AND DISCUSSION

It is well established that the slowing dynamics observed when the system is approaching the glass transition can be

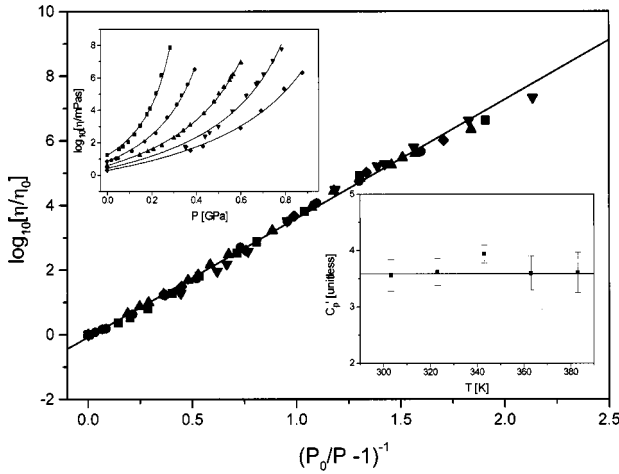


FIG. 1. Pressure dependence of the viscosity of salol for several temperatures ranging from 303.2 K (rectangles) to 383.2 K (diamonds). A full listing of temperatures can be found in Ref. 3. The data in the main area of the figure are normalized by plotting reduced viscosity against reduced pressure, as described in the text. The non-normalized data are shown in the top left-hand inset. Solid lines are one-parameter fits with Eq. (2), as described in the text. The bottom right-hand inset presents the temperature dependence of C'_p .

analyzed in terms of viscosity, in an analogous way as in terms of relaxation time. In view of the above, the following relationship can be suggested to account for the viscosity pressure characteristic:

$$\log_{10} \eta = \log_{10} \eta_0 + \frac{C'_p P}{P_0 - P}, \quad (2)$$

where η_0 denotes the viscosity measured under atmospheric pressure and C'_p is the viscosity counterpart of C_p . For isothermal measurements starting from atmospheric pressure, the value of η_0 is known and Eq. (2) has only two unknown parameters C'_p and P_0 which can be determined from fitting. Below, we argue that the effect of pressure on viscosity in salol and ortho-terphenyl can be satisfactorily described by Eq. (2), which has two adjustable parameters.

Figure 1 illustrates application of Eq. (2) to the analysis of the pressure viscosity characteristic of salol measured at five temperatures ranging from 303.2 to 383.2 K. The bottom right-hand inset shows the values of C'_p determined from the fitting of the data with Eq. (2). There is a strong indication that, within the limits of experimental accuracy, C'_p can be regarded as a temperature-independent parameter. Therefore, the above values of C'_p have been averaged and the fitting has been repeated with fixed C'_p . The top left-hand inset to Fig. 1 shows the results of this one-parameter fitting of the data with Eq. (2) (solid lines). It can be concluded that the relationship examined provides a satisfactory phenomenological description of the data. This is in contrast to the previous analysis,³ where no expression suitable to fit the data for salol has been suggested.

A convenient way of analyzing the applicability of Eq. (2) to account for the experimentally observed viscosity pressure behavior is in terms of the reduced viscosity $\tilde{\eta}$ and reduced pressure \tilde{P} defined as

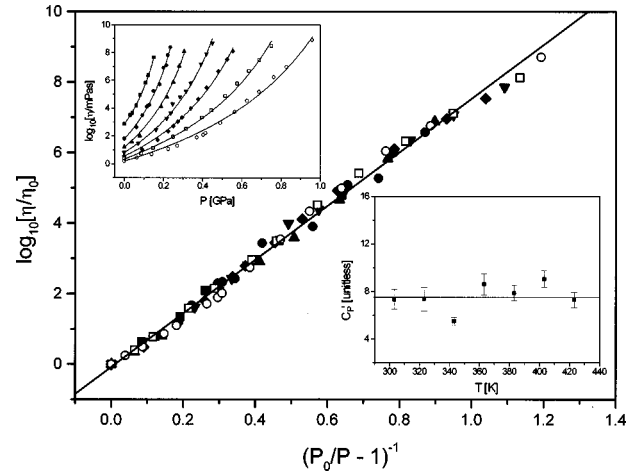


FIG. 2. Pressure dependence of the viscosity of ortho-terphenyl for several temperatures ranging from 303.2 K (solid rectangles) to 423.2 K (open circles). The data in the main area of the figure are normalized by plotting reduced viscosity against reduced pressure. The non-normalized data are shown in the top left-hand inset. The lines are one-parameter fits with Eq. (2). The bottom right-hand inset gives the temperature dependence of C'_p .

$$\tilde{\eta} = \frac{\eta}{\eta_0}, \quad (3)$$

$$\tilde{P} = \frac{P}{P_0 - P}. \quad (4)$$

The data in the main area of Fig. 1 are plotted as $\tilde{\eta}$ against \tilde{P} . It can be noticed that applying such coordinates adjusts the data measured at five different temperatures along a single straight line. This confirms that Eq. (2) is suitable to fit the data and that C'_p can be regarded as temperature independent. The latter statement implies that C'_p depends solely on the properties of a given glass former and does not depend on the thermodynamical condition. This is in contrast to the original temperature fragility index which is found to be pressure dependent.

A similar analysis is presented in Fig. 2 for ortho-terphenyl. Also in this case Eq. (2) proved to satisfactorily fit the data, in contrast to the free volume expression used previously for this effect.³ The bottom right-hand inset shows the values of C'_p determined for seven isotherms ranging from 303.2 to 423.2 K, from the two-parameter fitting of the data with Eq. (2). In the case of ortho-terphenyl, the values fluctuate in the vicinity of $C'_p \cong 7.5$ and does not exhibit such pronounced coincidence as was the case of salol, which can be assigned with larger experimental errors. The results of the one-parameter fitting of the data with Eq. (2) (solid lines) are shown in the top left-hand inset. The averaged value of C'_p has been fixed for the one-parameter fitting, similarly as was done in the case of salol. In the main area of Fig. 2, the scaling plot for the pressure viscosity data of ortho-terphenyl is presented.

Another important characteristic of a given glass former is the pressure of the ideal glass transition P_0 . Figure 3 shows the temperature dependence of P_0 for salol, determined from the two-parameter fitting of the pressure viscosity data with

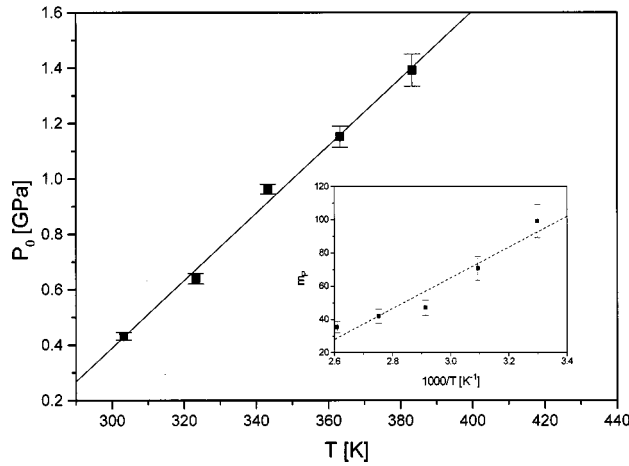


FIG. 3. Temperature dependence of the pressure of the ideal glass transition, P_0 , for salol. The inset shows the temperature characteristic of the pressure fragility index m_p defined for $P_g = P(\eta = 10^{10} \text{ mPa s})$.

Eq. (2). It can be concluded that the above characteristic can be regarded as approximately linear. Figure 4 presents the temperature dependence of P_0 for ortho-terphenyl, which has been determined the same way as in the case of salol. For ortho-terphenyl the pressure behavior of P_0 can be roughly described by a linear characteristic. The bottom right-hand inset shows the pressure behavior of P_0 for ortho-terphenyl determined from the one-parameter fitting of the data with Eq. (2) (the averaged value of C'_p has been fixed for the fitting). In this case, parabolic fit (dashed line) provides a very good approximation of the P_0 temperature characteristic.

Recently, Alba-Simionesco and co-workers¹⁰ have adapted Adam-Gibbs theory to the isothermal condition. They have pointed out that the same pressure fragility index $m_p = (d \log_{10} \eta / dP)_{P=P_g}$ is proportional to $(V_f + V_g \Delta \alpha \Delta \mu / S_c) / T$, where V_f and V_g are the free volume and volume at the glass transition, $\Delta \alpha$ is the expansivity jump, and $\Delta \mu$ is the potential energy of rearranging a molecule in a cooperatively rearranging region (CRR). The pressure fragility index has been introduced by analogy to its temperature counterpart¹¹ (here m_p is not normalized by T_g), as an alternative measure of the fragility of glass-forming liquids. It is suggested¹⁰ that m_p decreases with increasing T , if one assumes that the potential energy of a molecule in the CRR remains constant. The insets to Figs. 3 and 4 show the temperature dependence of the viscosity fragility index m_p [defined for $P_g = P(\eta = 10^{10} \text{ mPa s})$] for salol and ortho-terphenyl.

The above considerations lead to some indication as to the general form of the temperature-pressure viscosity ‘‘equation of state’’

$$\eta(T, P) = \eta_0(T) \exp \frac{C_p P}{P_0(T) - P}, \quad (5)$$

where $\eta_0(T)$ denotes the temperature characteristic of viscosity.¹² The main problem related to this temperature component is that there is no commonly accepted expression for $\eta_0(T)$. Equation (5) can serve as a base to create a ca-

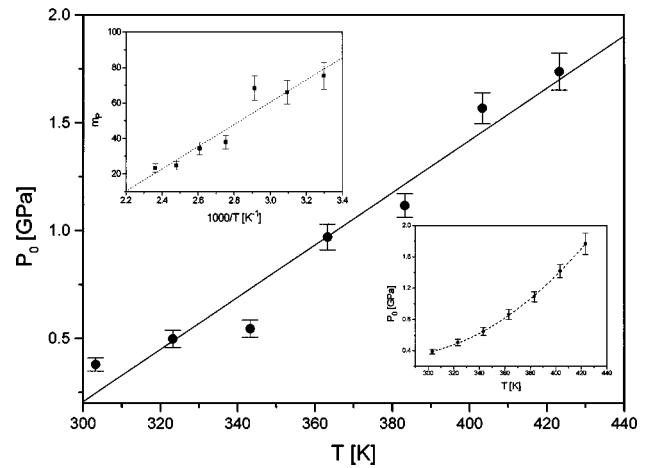


FIG. 4. Temperature dependence of the pressure of the ideal glass transition, P_0 , for orthoterphenyl. The characteristic presented in the bottom right-hand inset has been calculated from the one-parameter fitting of the data with Eq. (2). In the latter case the values of C'_p have been averaged and treated as a fixed parameter, as described in the text. The dashed line represents the parabolic fit to the data. The top left-hand inset shows the temperature characteristic of the pressure fragility index m_p defined for $P_g = P(\eta = 10^{10} \text{ mPa s})$.

nonical model of the processes observed in the glassy state, with physically interpretable parameters.

III. CONCLUSIONS

The pressure dependence of viscosity for salol and ortho-terphenyl is well reproduced, over considerable ranges of pressure (up to 1 GPa) and temperature (300–425 K), by the two-parameter relationship, analogous to that proposed previously for the relaxation-time–pressure behavior. Worth stressing is the fact that no phenomenological relationship has been proposed previously in case of salol. Similarly, the free volume expression applied previously to the data for ortho-terphenyl proved to be unsuitable to satisfactorily reproduce these data.

Particularly interesting is the fact that C'_p can be regarded as constant for a given glass former and does not depend on temperature. As a result, the pressure viscosity data of the glass former collected for different temperatures scale on a single master plot constructed by plotting reduced viscosity $\tilde{\eta}$ against reduced pressure \tilde{P} . Finally, the general form of the combined temperature-pressure dependence of viscosity can be derived on the basis of the presented phenomenology.

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