

Relative contributions of thermal energy and free volume to the temperature dependence of structural relaxation in fragile glass-forming liquids

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Structural relaxation of fragile glass-forming liquids in the vicinity of the glass transition were measured by dielectric spectroscopy, as a function of temperature and pressure. From the volume dependence of the relaxation times, we show that the effects of thermal and free volume fluctuations are comparable. The implication is that theoretical approaches in which intermolecular barrier heights are related to the local density are essential to formulating a theory of the structural dynamics of supercooled liquids.

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The understanding of the dynamics of transport properties and relaxation in glass-forming liquids remains a central issue of condensed matter physics.¹⁻⁸ A variety of experimental techniques, such as dielectric and mechanical spectroscopies, NMR, light scattering, etc., enable the relaxation properties of supercooled liquids to be probed over broad ranges frequency or time. The results from all such measurements unambiguously show that the increase of the structural (α -) relaxation time in the vicinity of the glass transition is super-Arrhenius.⁹

As temperature is reduced, the molecular motions of a supercooled liquid become more restricted, due to both the decrease of thermal energy and the increased molecular crowding.^{10,11} Thus the properties near T_g reflect both thermal and density effects. As emphasized by Ferrer *et al.*,⁹ the relevant question is whether the super-Arrhenius behavior near the glass transition at ambient pressure is governed primarily by the decreasing volume, the decreasing temperature, or both.

Obviously, a resolution of this issue is essential to formulating a satisfactorily complete theory of the glass transition. Recently, from high-pressure viscosity data for triphenyl phosphite (TPP) and glycerol, Ferrer *et al.*⁹ concluded that the super-Arrhenius behavior at atmospheric pressure is primarily due to temperature rather than density. In addition, these authors suggested that, except possibly at very high pressures, the glass transition is not a result of congestion due to a lack of free volume. More recently, Ngai *et al.*¹² measured the *o*-positronium lifetimes of various glass formers (glycerol, propylene glycol, and propylene carbonate) as a function of temperature. The data indicate that the “unoccupied” volume correlates with the dielectric α -relaxation time over a wide temperature range, implying that volume cannot be neglected in analyses of structural relaxation properties.

In this paper we present structural relaxation times near T_g over a wide range of thermodynamic variables [i.e., temperature (T), pressure (P), and volume (V)], for phenylphthalein-dimethylether (PDE) and poly[(phenyl glycidyl ether)-co formaldehyde] (PPGE). Our results demonstrate unequivocally the importance of fluctuations in both thermal energy and free volume for structural relaxation in supercooled liquids.

The α -relaxation times were determined from dielectric measurements as a function of temperature and pressure. Additionally, PVT measurements were carried out in order to deduce the volume dependence of τ_α .^{13,14} A detailed description of the experimental techniques can be found elsewhere.^{15,16}

In Figs. 1 and 2 is shown the respective variation of structural relaxation times with specific volume for PDE and PPGE. In both cases, the isobaric and isothermal curves diverge from each other. Although one can argue that specific volume is not necessarily proportional to the free volume, the fact that the former does not uniquely define τ is contrary to free volume models. Neither does thermal energy solely govern the relaxation times, although for a given volume change, τ_α is more influenced by temperature than by pressure. For example, in the case of PDE, pressure-induced changes in volume equivalent to a 50° temperature change cause τ_α to vary by almost three decades.

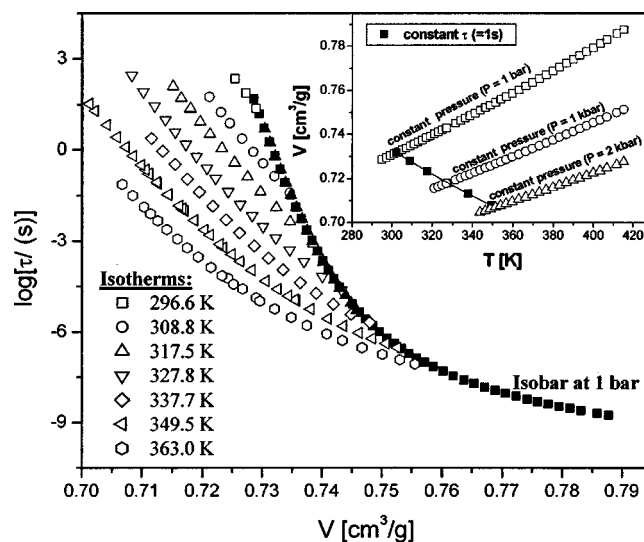


FIG. 1. Comparison of isothermal and isobaric dependences of the relaxation time on specific volume for PDE. The solid squares are the dielectric relaxation times measured at ambient pressure by Stickel (Ref. 20). The inset shows respective temperature variations of the specific volume at constant pressure and at constant relaxation time.

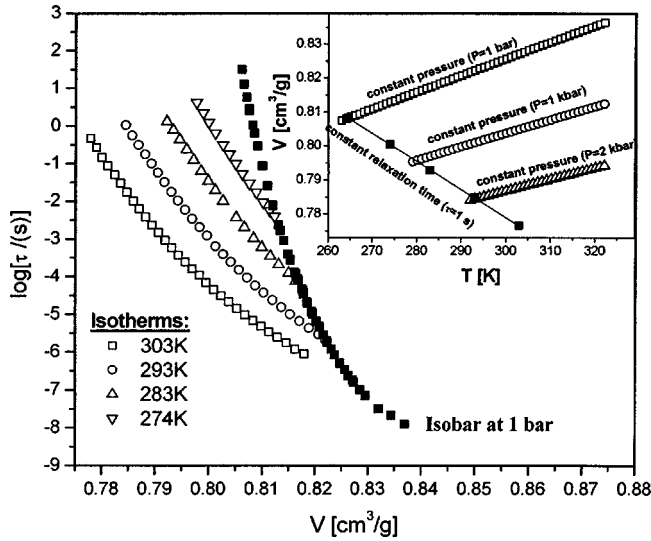


FIG. 2. Comparison of isothermal and isobaric dependences of the relaxation time as a function of specific volume for PPGE. The inset shows respective temperature variations of the specific volume at constant pressure and at constant relaxation time.

Since thermal energy and molecular packing are both important, assessment of the relative contributions of thermal energy and volume to the temperature dependence of τ_α is useful. One approach, proposed in Ref. 9, is from the ratio of the isochronic expansivity [$\alpha_\tau = -\rho^{-1}(\partial\rho/\partial T)_\tau$] to the isobaric expansivity [$\alpha_P = -\rho^{-1}(\partial\rho/\partial T)_P$]. A large ratio of $|\alpha_\tau/\alpha_P|$ implies that slowing down of the dynamics is mainly due to temperature, rather than density or volume. A ratio near unity, however, is expected if the contribution from both factors is significant.

This ratio was determined for PDE and PPGE using the data shown in the insets to Figs. 1 and 2. The results, $|\alpha_\tau/\alpha_P| = 1.25$ and 1.67 for PDE and PPGE, respectively, are close to unity, indicating that volume exerts a substantial influence on the supercooled dynamics at ambient pressure. In addition, as seen in the inset to the figures, this ratio increases for PDE from 1.25 to 1.43 and for PPGE from 1.67 to 2.4, as the pressure is increased from 0.1 MPa to 0.2 GPa. Thus, contrary to intuition as well as the suggestion in Ref. 9, thermal effects may actually become more important at elevated pressure.

An alternative way to define the direct contribution of volume to the temperature dependence of the relaxation times is from the ratio of the activation energy at constant volume, E_V , to the activation enthalpy at constant pressure, H_P .¹⁷ Note that at ambient pressure, the difference between E_V and H_P is the energy required to produce the requisite activation volume within the liquid. In order to calculate E_V/H_P , we analyze the temperature dependence of the structural relaxation times at constant volume,

$$E_V = \left[\frac{\partial \ln \tau}{\partial (T^{-1})} \right]_V, \quad (1)$$

and at constant pressure,

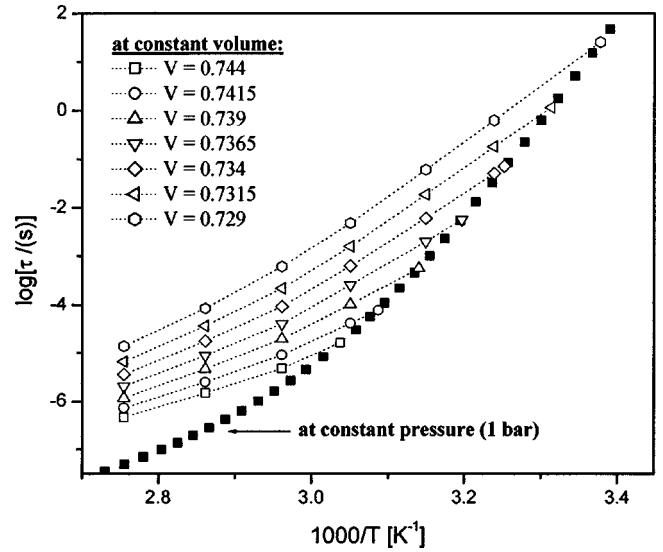


FIG. 3. Temperature dependence of the relaxation time for PDE at constant pressure and at constant volume.

$$H_P = \left[\frac{\partial \ln \tau}{\partial (T^{-1})} \right]_P. \quad (2)$$

The results, depicted in Figs. 3 and 4, yield $E_V/H_P = 0.52_5$ and 0.62_5 for PDE and PPGE, respectively. The value of E_V/H_P would be close to unity if the molecular motion were thermally activated and close to zero if dominated by density. Neither is the case, as this analysis shows again that both volume and thermal effects are important. These results agree qualitatively with the model of structural relaxation due to Pakula.¹¹ The general assumption made therein is to regard relaxation as a reflection of thermally activated processes, with activation energies which depend on local volume. As a consequence, molecules can jump into new sites provided they have sufficient energy and these sites are unoccupied.

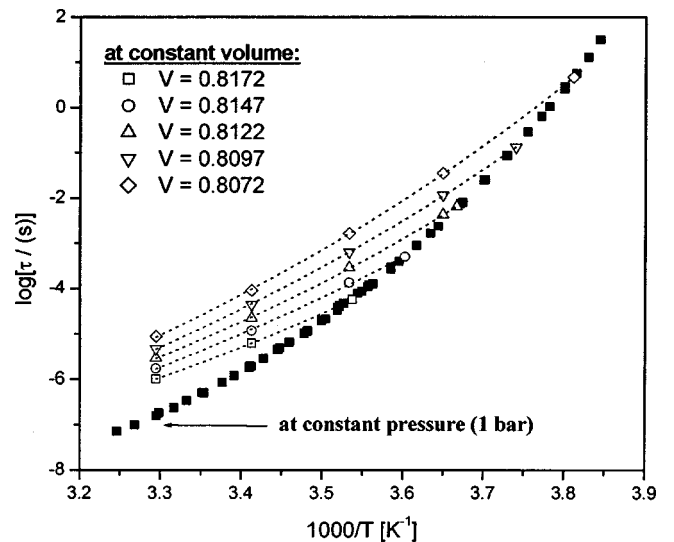


FIG. 4. Temperature dependence of the relaxation time for PPGE at constant pressure and constant volume.

TABLE I. Values of the ratios $|\alpha_T|/\alpha_P$ and E_V/H_P for various glass-forming liquids.

Glass formers	$ \alpha_T /\alpha_P$	E_V/H_P	Reference
PDE	1.25	0.52 ₅	herein
PPGE	1.67	0.62 ₅	herein
cresolphthalein-dimethylether	0.98		18
glycerol	17		9
diglycidylether of bisphenol A	1.8	0.6	19
<i>o</i> -terphenyl (OTP)		0.55	17
triphenylchloromethane/OTP mixture		0.45	17
triphenylomethane triglycidyl ether		0.63	17

In Table I we compare our results for PDE and PPGE with data for other common glass formers. It can be seen that, in general, volume exerts a significance influence on molecular mobility. The notable exception is glycerol, for which the

dominant role of temperature may reflect the presence of hydrogen bonding. Strong thermal fluctuations are required to overcome these bonds and allow relaxation to proceed.

Pace recent literature,⁹ we conclude that temperature is not the dominant control variable for structural relaxation. The experimental results presented herein show definitively that fluctuations in both thermal energy and free volume contribute to the dynamics of supercooled liquids. Although exceptions to this general behavior may occur, they likely entail unusual chemical interactions, such as strong hydrogen bonding. Thus theoretical efforts cannot focus exclusively on activated dynamics or on free volume. Consideration must be given to both mechanisms, such as in models in which the barrier heights are quantitatively related to the local density.

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