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Letter to the Editor

# The Avramov model of structural relaxation

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**Abstract**

The Avramov model, an entropy-based description of the effects of temperature and pressure on structural relaxation times, assumes separability of these two dependences. This implies that the fragility of glass-formers is independent of pressure. Herein we show that experimental results for polymethyltolylsiloxane are at odds with this assumption. By introducing a linear increase of the coordination number of the liquid state with pressure, the model can be modified, enabling good agreement with experiment to be achieved.

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**1. Introduction**

Structural relaxation of glass-formers is an issue of central importance to condensed matter physics; thus, studies of the dynamics of polymers and small molecule glasses near their glass transition are quite prevalent. The past few years has seen enormous growth in the use of hydrostatic pressure as an experimental variable in such studies [1–29]. Obviously, the status of pressure as a fundamental thermodynamic quantity motivates these efforts. Moreover, there are specific reasons for applying elevated pressure:

(i) An understanding of the relationship between local structure and relaxation properties should include the effects of pressure. As an example, polymethylphenylsiloxane (PMPS) and polytolylsiloxane (PMTS) have very similar chemical structures. However, while their ambient pressure properties, such as the shape of the relaxation function and fragility, are virtually identical, the pressure dependences of the dynamics for these two polymers are very different [29,30].

(ii) Most models for the dynamics of glass-formers embody one of two contrary viewpoints. Free volume approaches posit the accumulation of unoccupied volume as the basic relaxation mechanism, with congested passage through low-energy pathways in configurational space governed by packing considerations [31–35]. The alternative point of view is that temperature is the dominant control variable, with relaxation involving

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thermally activated surmounting of potential barriers [25,36]. Both assumptions cannot be entirely correct, and pressure studies allow the relative contribution of volume and thermal energy to be quantified.

(iii) Finally, advantage can be taken of the different pressure dependences of relaxation times to allow overlapping resonances to be resolved. In this case, pressure is just a tool to deconvolute spectra.

The burgeoning interest in measurements at elevated pressure has renewed interest in analytical expressions for the combined effects of temperature and pressure. These experiments increase enormously the amount of information obtained; thus,  $\tau(T, P)$  relationships that merely parameterize the data can be useful. More importantly, models for the effect of pressure are necessary to interpret the data, as well as to guide experimentalists.

A number of different models for combined pressure and temperature dependences of structural relaxation have been proposed. Fytas and coworkers generalized the Vogel–Fulcher equation to include the effects of temperature and pressure [37]. However, their expression predicts a linear dependence of  $T_g$  on pressure, which is at odds with experimental data [30,38]. From free volume considerations, Cohen and Grest [33] derived an expression for  $\tau(T, P)$ . Although their equation describes temperature dependences at ambient pressure for many glass-formers, the accuracy is poor for the pressure dependence of  $\tau$ . The defect diffusion model of Bendler and Shlesinger [39] has recently been extended to include the effect of pressure [26]. Casalini et al. [40] extended the Adam–Gibbs model, and within the framework of configurational entropy considerations, obtained a  $\tau(T, P)$  relationship. Successful application of this extended Adam–Gibbs model to data for epoxy resins has been demonstrated [16,41]. We should note that this model formally predicts that fragility must be pressure dependent.

Avramov has recently proposed an entropy-based model, which provides an analytical description of the structural relaxation times as a function of temperature and pressure [42–44]. The model is based on the hypothesis that the cooperative motion underlying structural ( $\alpha$ -) relax-

ation is thermally activated. Assuming a Poisson distribution of the local energy barriers, Avramov derived a relationship between the  $\alpha$ -relaxation time and the system entropy:

$$\log \tau = \log \tau_0 + \frac{E_{\max}}{\sigma_r} \exp \left[ -\frac{2(S - S_r)}{ZR} \right]. \quad (1)$$

From thermodynamic consideration, the following relation obtains:

$$\log \tau = \log \tau + 13 \left( \frac{T_r}{T} \right)^a \left( 1 + \frac{P}{\Pi} \right)^b \quad (2)$$

with  $b = (2\kappa_0 V_m / ZR)\Pi = a(\kappa_0 V_m / C_p)\Pi$ , where  $\kappa_0$  is the volume expansion coefficient at ambient pressure,  $C_p$  the specific heat capacity,  $V_m$  the molar volume and  $\Pi$  is a constant. The parameter  $Z$  represents the number of available pathways for local relaxation of a polymer segment, reflecting the short range structure [43]. Although  $Z$  cannot be directly determined from experiment, it is expected to be proportional to the coordination number of the liquid lattice [45]. The exponent  $a$  is proportional to the ratio of the heat capacity and the coordination number,  $a = 2C_p / RZ$ , with  $C_p$  and  $Z$  assumed to be independent of pressure.

In Refs. [30,38,46] it was demonstrated that for three polymers, PMPS, poly[(phenyl glycidyl ether)-co-formaldehyde] (PPG), and diglycidyl-ether of bisphenol A (DGEBA), Eq. (1) accurately described experimental relaxation times covering a broad range of temperature and pressure. Moreover, for PMPS, the required material parameters were available, whereby a connection between the Avramov parameters and thermodynamic properties of the material could be established [30].

In this paper we use the Avramov model to analyze the combined temperature and pressure dependences of structural relaxation times for PTMS. We show that an accurate description of  $\tau(T, P)$  for PMTS requires modification of Eq. (2). The physical basis for this modification is discussed.

## 2. Results and discussion

An important parameter quantifying the temperature dependence of structural relaxation time

is the fragility, commonly defined as the steepness index [47]:

$$m = \left. \frac{d \log \tau}{T_g/T} \right|_{T=T_g} \quad (3)$$

In terms of the Avramov parameters in Eq. (2), the steepness index is given by

$$m = a(\log \tau(T_g) - \log \tau_0), \quad (4)$$

where by convention,  $\tau(T_g) = 1$  s. This relation makes clear the lack of any explicit dependence of fragility on pressure, which assumes  $C_p$  and  $Z$  are constant. Thus, Eq. (2) is limited to the description of temperature and pressure dependences for glass-formers with constant values of fragility. Examples of the latter include PMPS [30], PPG [38], and DGEBA [46].

Herein we employ the Avramov model to describe  $\tau(P, T)$  data for another polymer, PTMS. Dielectric measurements at pressures up to 250 MPa revealed the fragility of this material to be inversely proportional to pressure [29]. Analysis of isotherms using the Vogel–Fulcher relation yields  $dm_T/dP = -0.03 \text{ MPa}^{-1}$ , with  $m = 85$  at atmospheric pressure [29]. As a consequence of the lack

of separability of the temperature and pressure dependences, Eq. (2) is incapable of describing the experimental results.

We can modify Eq. (4) to account for the decrease of fragility with pressure by introducing an additional parameter  $c$

$$m = (a + cP)(\log \tau(T_g) - \log \tau_0). \quad (5)$$

This leads to a modified expression form of the Avramov relation for the structural relaxation time

$$\log \tau = \log \tau_0 + 13 \left( \frac{T_r}{T} \right)^{(a+cP)} \left( 1 + \frac{P}{\Pi} \right)^b. \quad (6)$$

In Fig. 1 we show the fit of Eq. (6) to the dielectric relaxation times of PTMS, with  $\tau_0 = 1.6(\pm 0.4) \times 10^{-10}$  s,  $a = 8.5 \pm 0.1$ ,  $c = -4.0 \times (\pm 0.2) \times 10^{-3} \text{ MPa}$ ,  $T_r = 252.1 \text{ K} \pm 0.2$ ,  $b = 2.3 \pm 0.1$ , and  $\Pi = 205 \text{ MPa} \pm 8$ . As can be seen, excellent agreement is achieved. Using Eq. (5) with  $\tau(T_g) = 1$  s, we obtain  $-0.039 \pm 0.003 \text{ MPa}^{-1}$  for the pressure dependence of  $m$ . This is close to the result,  $dm/dP = -0.03 \text{ MPa}^{-1}$  [29], obtained from analysis of each isotherm using the Vogel–Fulcher equation [48].

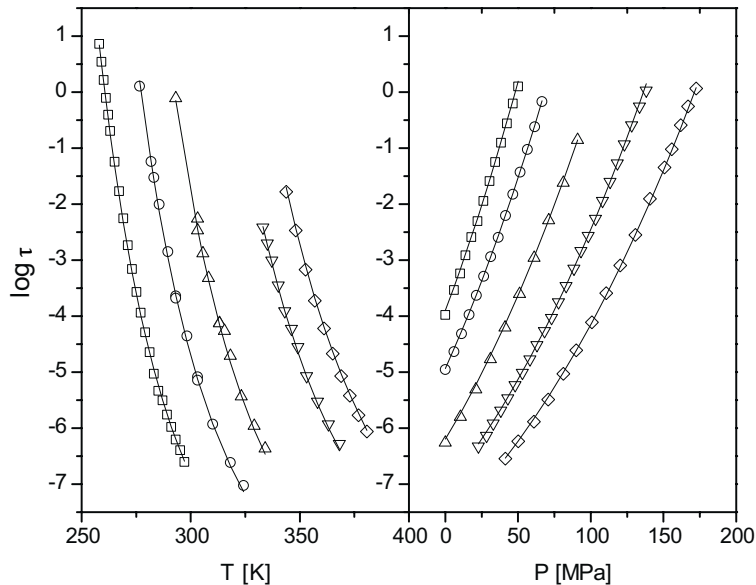


Fig. 1. Isobaric and isothermal dependences of segmental relaxation time in PMTS. The solid lines represent the fits to the data using Eq. (6).

This particular modification of the Avramov model implies that either the specific heat capacity or the coordination number of the liquid lattice varies with pressure,  $C_p/Z = (a + cP)R/2$ . If  $Z$  is pressure independent,  $dC_p/dP$  for PMTS is negative,  $\approx -0.1 \text{ JK}^{-1} \text{ mol}^{-1}/\text{MPa}$ . Data for the behavior of  $C_p$  under conditions of high compression are scarce; however, results for molecular glass-formers all indicate that  $C_p$  increases with pressure [49].

This implies that the fragility change induced in PMTS by pressure must reflect a change in  $Z$ . In fact, models [50,51] and simulations [52,53] of fluids invariably predict an increase in coordination number with pressure. Thus, our results are both plausible and qualitatively consistent with theory. The fragility change observed in PMTS is about 10% for a 250 MPa increase in pressure. The corresponding change in  $Z$  would be proportional. Although specific data for PMTS are lacking, the changes in coordination number necessary to account for the observed changes in fragility are of the correct magnitude [52,53].

Finally, we point out that this connection between fragility and coordination number is not unique to the Avramov model. A similar relationship is found in the landscape model of Vilgis [54]. Certainly, further efforts would be useful to establish the manner in which the relaxation dynamics of glass forming liquids reflect their local liquid structure.

### 3. Conclusions

The fragility of PMTS decreases with pressure. Such relaxation behavior is at odds with the separability of temperature and pressure effects implicit in the entropy model of Avramov. We demonstrate that a modification of the Avramov equation provides an accurate description of the combined temperature and pressure dependences of the  $\alpha$ -relaxation times. The pressure dependence of the fragility for PMTS deduced from the analysis is in agreement with a previous determination based on the Vogel–Fulcher equation. These results are consistent with the expected increase in the coordination number with pressure, thus sug-

gesting a connection between dynamics and the local liquid structure.

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