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Comment on "Correlations between isobaric and isochoric fragilities and thermodynamical scaling exponent for glass-forming liquids"

R. Casalini
Chemistry Department, George Mason University, Fairfax, Virginia 22030, USA
and Naval Research Laboratory, Chemistry Division, Code 6120, Washington, D.C. 20375-5342, USA

C. M. Roland
Naval Research Laboratory, Chemistry Division, Code 6120, Washington, DC 20375-5342, USA

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For nonassociated, glass-forming liquids and polymers, thermodynamic scaling of structural relaxation times and viscosities is an empirical fact, demonstrated by various groups for dozens of materials. The P and T invariance of the isochoric fragility follows directly from this scaling. Apparent inconsistencies with these statements were reported recently by Grzybowski *et al.* [A. Grzybowski, K. Grzybowska, J. Zioło, and M. Paluch, Phys. Rev. E **74**, 041503 (2006)]; however, the putative inconsistencies arise from use at higher pressures of parameters to correlate the isobaric and isochoric fragilities that are valid only for ambient pressure.

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Recent works [1–4] have shown that α- (structural) relaxation times, τ, conform to a thermodynamic scaling expressed as

$$\tau = \Im(TV^{\gamma}), \tag{1}$$

where T is temperature, V the specific volume, γ a material constant, and $\Im$ represents an unknown function (for a review, see [5]). A similar result is also found for the viscosity of glass-forming materials [6]. From Eq. (1) and the definitions of the isochoric, $m_V = \partial \log_{10}(\tau)/\partial(T_g/T)|_{V=const,T_g}$ and isobaric, $m_P = \partial \log_{10}(\tau)/\partial(T_g/T)|_{P=const,T_g}$ fragilities, it follows that [7]

$$m_V = \left.\frac{\partial \log_{10}(\tau)}{\partial(\Gamma_g/\Gamma)}\right|_{\Gamma_g}, \tag{2}$$

where $\Gamma = TV^{\gamma}$ and $\tau(\Gamma_g)$ is a constant (typically 100 s), and

$$m_V = \frac{m_P}{1 + \gamma \alpha_P T_g}, \tag{3}$$

where α_P is the isobaric thermal expansion coefficient at the glass transition temperature T_g. Two straightforward conclusions follow: From Eq. (2), if the scaling [Eq. (1)] is valid, then m_V must be a constant. From Eq. (3), since $\alpha_P T_g$ decreases with P [as is true for normal liquids, but not necessarily for strongly H-bonded materials (e.g., water)], then m_P decreases with P.

In a previous publication [8], we showed that for nonassociated liquids and polymers a correlation exists between the isobaric fragility *at atmospheric pressure* m_{P_0} and the isochoric fragility, which can be described by a linear equation

$$m_{P_0} = a + b\, m_V, \tag{4}$$

with a and b constants. Although the two fragilities strongly correlate, we pointed out "Of course, this is only a general pattern, rather than a strict relationship" [8]. Nevertheless, Eq. (4) has a number of important consequences. First, materials with large isobaric fragilities, measured for the usual condition of atmospheric pressure, have dynamics dominated more by T than by V. Second, any correlation of other properties with m_{P_0} translates directly into a correlation with m_V. Third, there exists an inverse correlation, described as "approximately linear behavior" [8], between the scaling parameter γ and m_V. The latter result follows from Eqs. (3) and (4) to the extent that $\alpha_{P_0} T_{g_0}$ does not vary much among different materials; such constancy is known as the empirical Boyer-Bondi rule [9], but it is only approximately valid [10]. We have shown for propylene carbonate and decahydroisoquinoline, which have large m_V, some departure from a linear of correlation of γ and $1/m_V$ [11].

In a recent paper, Grzybowski *et al.* [12] suggested that the two correlations presented in Ref. [8] are not entirely correct, thus calling into question the validity of the thermodynamic scaling of α-relaxation times [Eq. (1)]. The purpose of this paper is to clarify any confusion arising from these statements.

Grzybowski *et al.* [12] state: "The correlation [Eq. (4)] should be valid with the same parameters at any pressure." But since m_V is a constant and m_P varies with pressure [5,13], the correlation [Eq. (4)] *must change with pressure*. Specifically, for nonassociated liquids and polymers, since m_P decreases with P, either the parameter a or b must decrease with P. Therefore the hypothesis that a and b are independent of pressure cannot be reconciled with Eq. (1).

This hyphothesis led Grzybowski *et al.* to two potentially misleading conclusions [12]: "The isochoric fragilities obtained from the correlation (i) [Eq. (4)] at ambient and elevated pressures are different." As pointed out above, the isochoric fragility of nonassociated liquids does not change with pressure [7]. And "$\gamma^{(corr)}$ calculated from the correlation (ii) at pressures of 0.1 MPa and 0.6 GPa differ," but the parameter γ is a pressure-independent material constant (otherwise the thermodynamic scaling has no meaning) [1–6].

These problems arise in Ref. [12] from applying Eq. (4) to high pressure data using values of the parameters a and b reported in Ref. [8] *for atmospheric pressure*.

Grzybowski *et al.* [12] state: "it is worth noticing that correlation (ii) should not be applied for H-bonded systems." This deviation was illustrated in Fig. 3 of Ref. [8] with data for glycerol and sorbitol. More generally, Eq. (1) fails for H-bonded materials, as was shown for water and oligomeric polypropylene glycol [6], in turn invalidating Eqs. (3) and (4).

Finally, statements in Ref. [12] might be misconstrued as indicating that the quantity $\Gamma = T^{-1}V^{-\gamma}$ could be independent of pressure; however, such constancy is thermodynamically untenable.

We hope that this Comment to the paper of Grzybowski *et al.* helps to elucidate the origin of the apparent inconsistencies presented therein.

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