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

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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. Zioł, 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 $\alpha$- (structural) relaxation times, $\tau$, conform to a thermodynamic scaling expressed as

$$\tau = \tilde{\tau}(TV\gamma),$$  
(1)

where $T$ is temperature, $V$ the specific volume, $\gamma$ a material constant, and $\tilde{\tau}$ 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, $m_V=\left.\partial \log_{10}(\tau)/\partial(Tg/T)|_{Vconst,Tg}$ and isobaric, $m_P=\left.\partial \log_{10}(\tau)/\partial(Tg/T)|_{Pconst,Tg}$ fragilities, it follows that [7]

$$m_V = \left.\frac{\partial \log_{10}(\tau)}{\partial(Tg/T)}\right|_{Vconst,Tg},$$  
(2)

where $\Gamma = TV\gamma$ and $\tau(Tg)$ is a constant (typically 100 s), and

$$m_V = \frac{m_P}{1 + \gamma \alpha P Tg},$$  
(3)

where $\alpha P$ is the isobaric thermal expansion coefficient at the glass transition temperature $Tg$. 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 $\alpha P Tg$ 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 $m_{P0}$ and the isochoric fragility, which can be described by a linear equation

$$m_{P0} = a + b m_V,$$  
(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 $m_{P0}$ translates directly into a correlation with $m_V$. Third, there exists an inverse correlation, described as “approximately linear behavior” [8], between the scaling parameter $\gamma$ and $m_V$. The latter result follows from Eqs. (3) and (4) to the extent that $\alpha P Tg$ 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 decalcohol-disequino-line, which have large $m_V$, some departure from a linear of correlation of $\gamma$ 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 $\alpha$-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 hypothesis 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 $\gamma$ 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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