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

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Our recent paper [A. Grzybowski, K. Grzybowska, J. Zioło, and M. Paluch, Phys. Rev. E **74**, 041503 (2006)] tested the correlations between isobaric and isochoric fragilities, m_P and m_V, as well as the scaling exponent γ under elevated pressure conditions. The preceding paper [R. Casalini and C. M. Roland, Phys. Rev. E **76**, 013501 (2007)] is a Comment by the authors of the correlations originally determined for atmospheric pressure. In this Reply we present our point of view on criticisms contained in the Comment. We clarify and maintain our previously drawn conclusions.

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The theses of our recent paper [1], where we have shown some inconsistencies with two correlations between isobaric and isochoric fragilities, m_P and m_V, as well as the scaling exponent γ, at elevated pressure, and moreover failure of the thermodynamic scaling in the case of some hydrogen-bonded systems, have been questioned [2] by the authors who originally suggested the correlations [3]. Therefore, we need to clarify again the purpose and results of that paper.

We would like to emphasize that we were fully aware that the coefficients m_0, a, γ_0, and b of the correlations (i) and (ii) were determined by Casalini and Roland [3,4] for atmospheric pressure: (i) $m_P=m_0+am_V$, (ii) $\gamma=\gamma_0+bm_V^{-1}$, where γ is the scaling exponent which is a material constant used as a parameter of the thermodynamic scaling of structural relaxation times τ,

$$\log_{10}(\tau) = J(\Gamma), \quad \Gamma = T^{-1}V^{-\gamma}. \tag{1}$$

We indicated that fact by appropriate references to their papers as well as by writing that "the isobaric fragilities m_P have been calculated at atmospheric pressure." Moreover, the question whether such discovered correlations can be really independent of thermodynamic conditions at least for nonassociated liquids and polymers just induced us to consider their validity under high pressure. The main goal of our previous paper [1] was to decide the matter. We are convinced that only the thermodynamic universality can make the correlations (i) and (ii) useful and essential tools for studying the thermodynamic scaling, otherwise there is a risk that they can be improperly used, and then one should remember that they are limited. Considerations presented in our paper [1] were partially presented as a proof by contradiction, and maybe that is the reason that a misunderstanding arose. It means that we assumed, for the sake of argument, that the correlations (i) and (ii) are valid under any thermodynamic conditions with their parameters determined for atmospheric pressure. As we expected, we found then that the correlations cannot be entirely correct. In that proof we used the facts that the isobaric fragility generally depends on pressure while the isochoric fragility is rather pressure independent, and that the exponent γ should be a material constant also independent of pressure so that the thermodynamic scaling works well. Consequently, we concluded that "To sum up, since $m_P(P) \neq \text{const}$ and $m_V(P)=\text{const}$, the parameters (m_0 and a) of correlation (i) should be pressure-varying functions, $m_0(P)$ and $a(P)$. However, then the universality of correlation (i) is broken because its parameters become dependent on thermodynamic conditions" and "correlation (ii) seems to be universal, because if $m_V(P)=\text{const}$, then γ is also pressure independent." Therefore, Casalini and Roland in their Comment actually present the same arguments for the pressure dependence of the parameters of correlation (i) and the pressure independence of the parameters of correlation (ii). Those authors view some of our statements as potentially misleading conclusions, while they are simply contradictions reached as a consequence of our proof by contradiction.

We are grateful for the Comment authors' remark about the pressure dependency of the quantity Γ [Eq. (1)]. We appreciate the fact that the statement of the pressure independence of Γ might be misconstrued by a reader, especially, who does not know of the idea of the thermodynamic scaling. Of course, the meaning of the statement is that the quantity $\Gamma=T^{-1}V^{-\gamma}$ is not *explicitly* pressure dependent, and exactly such has been our intention.

The second important issue considered in our previous paper is the problem of the validity of the thermodynamic scaling for any materials. At first we would like to note that we did not call into question the validity of the thermodynamic scaling as a result of the inconsistency with the correlations, as has been stated by the authors of the Comment [2]. On the contrary, we required the pressure independence of the material constant γ for the validity of the thermodynamic scaling in the case of van der Waals liquids and polymers as has been already mentioned. However, in the case of H-bonded systems we explained that the obtained "inconsistency that the scaling exponent $\gamma^{(corr)}$ derived from the correlation (ii) with $m_V^{(corr)}$ is strongly dependent on P" need not be a strange result because "searches for conditions which would enable the required pressure independence of the scaling exponent γ can be even at variance with intrinsic properties of these materials. Their molecular structures and H-bonded networks especially vary with changing P, V, and

T, because the thermodynamic conditions strongly affect the degree of H-bonds." In addition we illustrated (in Fig. 3 in Ref. [1]) the problem with the thermodynamic scaling of dielectric data for dipropylene glycol which cannot be plotted on one master curve defined by Eq. (1). The illustration was meant to argue that failure of the thermodynamic scaling for H-bonded systems prevents any reasonable use of the correlations for the materials.

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[1] A. Grzybowski, K. Grzybowska, J. Zioło, and M. Paluch, Phys. Rev. E **74**, 041503 (2006).
[2] R. Casalini and C. M. Roland, Phys. Rev. E **76**, 013501 (2007).
[3] R. Casalini and C. M. Roland, Phys. Rev. E **72**, 031503 (2005).
[4] R. Casalini, S. Capaccioli, and C. M. Roland, J. Phys. Chem. B **110**, 11491 (2006).