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

A. Grzybowski, K. Grzybowska, J. Zioło, and M. Paluch
Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland

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Two correlations concerning the isobaric and isochoric fragilities, m_P and m_V, as well as the scaling exponent γ reported by Casalini and Roland [Phys. Rev. E **72**, 031503 (2005)] have been examined for several van der Waals and hydrogen-bonded glass formers. It has been pointed out that the correlations lead to some serious inconsistency with the exponent γ, which is expected to be a constant dependent only on material, but varies also on pressure if experimentally found pressure dependences of m_P are taken into account. This problem could be solved in the case of van der Waals liquids, but then at least one of the correlations becomes dependent on thermodynamic conditions, and consequently, loses its universality. However, some H-bonded systems, due to properties of hydrogen bonding, have been well argued not to be included to determine the correlations independently of thermodynamic conditions. Furthermore, it has been noticed that another correlation concerning the fragility, between m_P and the structural relaxation peak breadth, yields discrepancies in comparison with results of experiments under elevated pressure.

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Thermodynamic scaling of molecular dynamics in the vicinity of the glass transition has been recently studied by several groups [1–7]. This idea is very appealing because it enables an attempt at finding a universal description of relaxation phenomena of all supercooled liquids on the basis of a generalized form of the Lennard-Jones (LJ) potential. One can expect that such an approach facilitates answering different important questions *inter alia* how temperature T and specific volume V influence on the structural relaxation near the glass transition. The first interesting results in this area have been obtained for a typical van der Waals liquid. Analyzing inelastic neutron scattering on *ortho*-terphenyl (OTP) Tölle [8] has observed that the use of the well-known LJ potential with its repulsive and attractive parts proportional to r^{-12} and r^{-6}, respectively, seems to be sufficient to describe molecular dynamics of the van der Waals liquid. This assumption enabled him to express relaxation times in terms of $T^{-1}V^{-4}$. This has been applied by Dreyfus *et al.* [1] to plot rotational relaxation times for different isotherms obtained from light-scattering data for OTP onto one master curve. It is worth mentioning that the approach can be *de facto* treated as density scaling of energy barriers of different dynamic processes.

Among others Casalini and Roland [3] have pointed out that thermodynamical scaling found for OTP is generally not valid for other glass formers. Therefore, they have proposed a generalized quantity $\Gamma = T^{-1}V^{-\gamma}$ independent of pressure which could replace a variable T. Consequently, a relaxation time has been expressed as a function of Γ

$$\log_{10}(\tau) = J(\Gamma). \tag{1}$$

The scaling quantity Γ can be followed from the generalized LJ potential [9] with its modified repulsive and attractive parts proportional to $r^{-3\gamma}$ and $r^{-3\gamma/2}$, respectively. The scaling exponent γ is a material constant, and it can be interpreted as an indicator of "softness" of an intermolecular repulsive potential. Moreover, the form of the quantity Γ suggests that the parameter γ reflects the relative thermal and volume effect on molecular dynamics. That means if γ decreases to zero, then Γ tends to rely more on T implying the intermolecular free volume contribution will decrease and the thermal activation influence will increase.

The dependence of the relaxation time [Eq. (1)] leads to the rescaled definition of the fragility $m = d\log_{10}(\tau)/d(\Gamma/\Gamma_g)|_{\Gamma=\Gamma_g}$ where Γ_g is a value of the scaling quantity Γ for the glass transition. Then, the isochoric and isobaric fragilities can be redefined [14] by $m_V = \partial\log_{10}(\tau)/\partial(\Gamma/\Gamma_g)|_{\Gamma=\Gamma_g}$ and $m_P = \partial\log_{10}(\tau)/\partial(\Gamma/\Gamma_g)|_{\Gamma=\Gamma_g}(1+\gamma\alpha_P T_g)$, respectively, where α_P is the isobaric thermal volume expansivity at T_g. Taking into account these representations of fragilities as well as definitions of the isochoric activation energy $E_V = R\,\partial\ln(\tau)/\partial T^{-1}|_{V=\text{const}}$ and the isobaric activation enthalpy $H_P = R\,\partial\ln(\tau)/\partial T^{-1}|_{P=\text{const}}$, the following relations have been derived [4,10]

$$\left.\frac{E_V}{H_P}\right|_{T=T_g} = \frac{m_V}{m_P} \tag{2a}$$

and

$$\frac{m_V}{m_P} = \frac{1}{1+\gamma\alpha_P T_g}. \tag{2b}$$

Recall that the ratio of E_V/H_P according to its definition [11] can be expressed in terms of the isobaric α_P and isochronic α_τ thermal volume expansivities as $(1+\alpha_P/|\alpha_\tau|)^{-1}$ with no scaling assumptions [12]. Using Eq. (2a) one can determine which of the thermodynamical variables, temperature or volume, becomes more important in controlling molecular dynamics of an examined material. If the quotient from Eq. (2a) approaches to 1, i.e., if $m_V = m_P$, then it can be determined that thermal activation play a decisive role in dynamic behaviors. On the other hand, the dynamics is mainly governed by intermolecular free volume if m_V/m_P approaches 0 due to m_V decreasing towards zero. Taking into account Eq.

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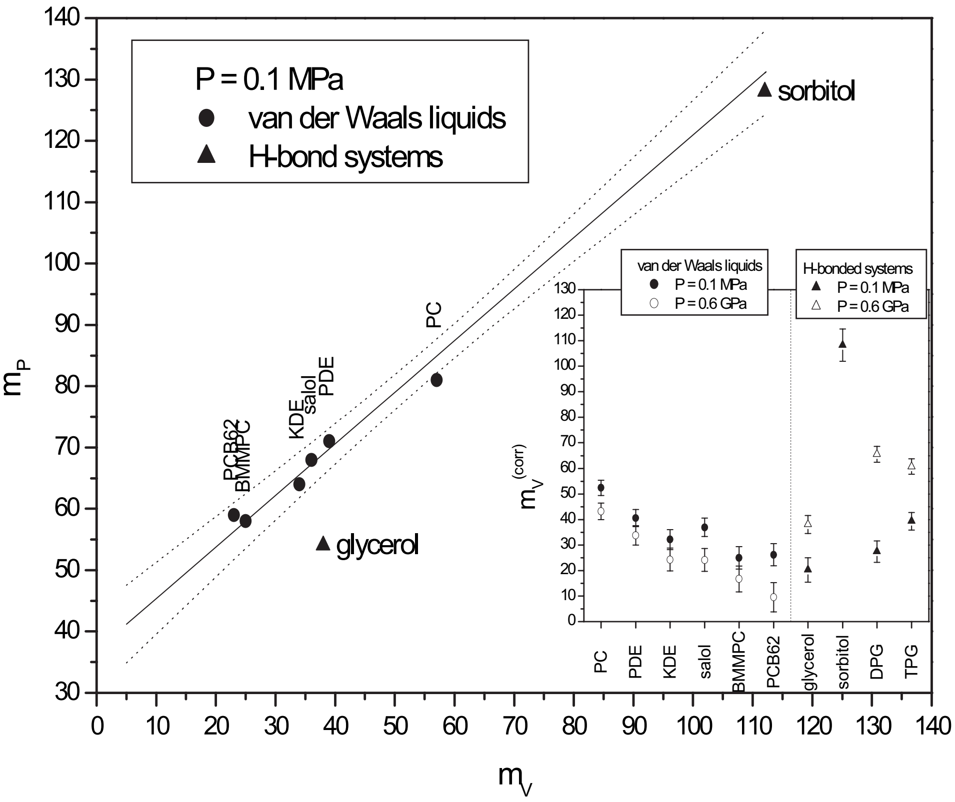

FIG. 1. Isobaric fragility m_P vs isochoric fragility m_V, both of them obtained experimentally (see Table I), for several van der Waals (●) and hydrogen-bonded (▲) glass formers. The solid line represents the correlation (i) with parameters taken from Ref. [10]. The dotted lines indicate confidence intervals for the correlation (i) which are determined from data shown by Fig. 2 in Ref. [10] assuming confidence limits equaled 0.95 and using correlation coefficient equaled 0.95 reported in Ref. [10] for the correlation (i). The inset shows isochoric fragilities $m_V^{(corr)}$ collected in Table I and their confidence intervals which are obtained from the correlation (i) at ambient and elevated pressure.

(2b) and the empirical rule [13,14] $\alpha_P T_g \approx$const, the scaling exponent γ is considered as a measure of the relative degree to which temperature and density control the dynamics [10].

The significance of Eqs. (2a) and (2b) have provoked Casalini and Roland to further search for more universal correlations between the isobaric and isochoric fragilities, as well as intrinsic properties of scaling, such as the exponent γ. Analyzing data from about thirty materials, including van der Waals glass formers, polymers, and hydrogen-bonded systems, they have suggested [10] two important correlations:

(i) *the linear correlation between the isobaric and isochoric fragilities*

$$m_P = m_0 + a m_V,$$

(ii) *the inverse linear correlation between the exponent* γ *and the isochoric fragility*

$$\gamma = \gamma_0 + b m_V^{-1},$$

where m_0=37±3, a=0.84±0.05, γ_0=−1.042, b=217, and are constant parameters of linear regression while the isobaric fragilities m_P have been calculated at atmospheric pressure. The parameters γ_0 and b are taken from Ref. [15].

In this paper, we examine whether the correlations (i) and (ii) are valid under high pressure conditions. Such tests seem to be essential for checking the suggested universality of the thermodynamical scaling. Herein we discuss whether this description can be applied both for van der Waals glass formers as well as H-bonded systems.

In order to check the correlations (i) and (ii), we have analyzed several van der Waals glass formers considered by Casalini and Roland [10]. The correlations are followed quite well at ambient pressure for this group of materials (Fig. 1), although experimentally obtained exponents γ are slightly outside of confidence intervals of the correlation (ii) for a half of the van der Waals materials tested by us (see Fig. 2), i.e. for propylene carbonate (PC), cresolphthalein-dimethylether (KDE), and 1,1'-di(4–methoxy-5–methylphenyl)cyclohexane (BMMPC). Using experimentally obtained values for m_P at atmospheric pressure [16] one can note that the isochoric fragilities $m_V^{(corr)}$, derived from the correlation (i) with its parameters m_0 and a found [10] at 0.1 MPa, correspond quite well with the experimental values of m_V (see Table I and Fig. 1). If the correlations (i) and (ii) were universal, they should be independent of thermodynamical conditions, and therefore, the correlations should be valid with the same parameters at any pressure. However, the isobaric fragility generally is pressure dependent, $m_P(P)$. For many van der Waals glass formers it has been found that m_P decreases with increasing pressure [4,16]. This fact and correlation (i) implicate that m_V must also change with P. In accordance with the correlation (ii), if

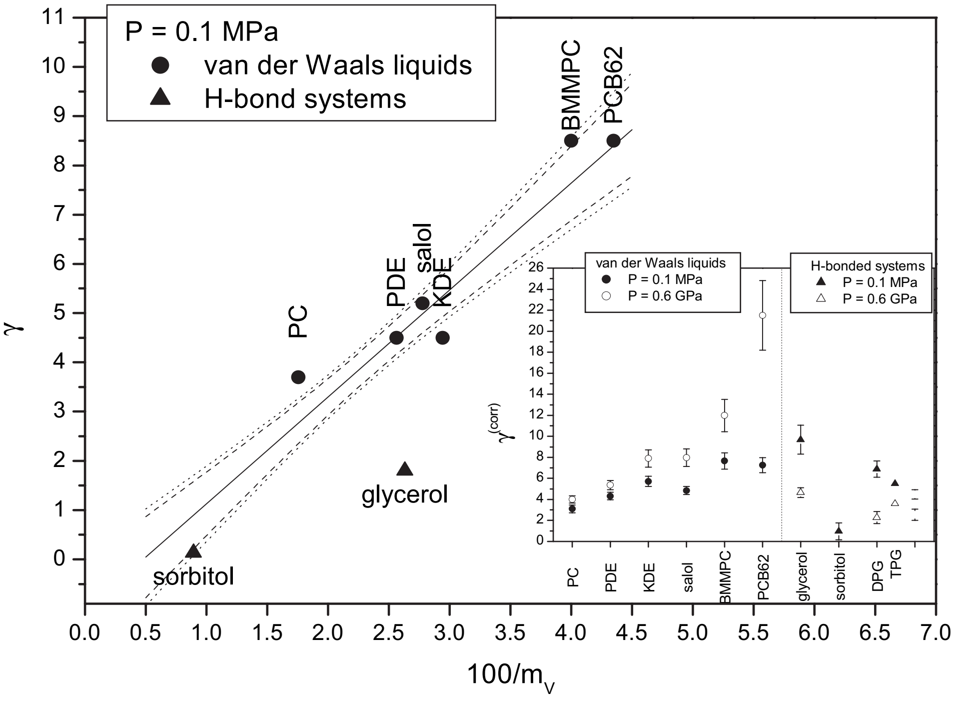

FIG. 2. Scaling exponent γ as a function of m_V^{-1}, both of them obtained experimentally (see Table I), for several van der Waals (●) and hydrogen-bonded (▲) glass formers. The solid line represents the correlation (ii) with parameters taken from Ref. [15]. The dashed and dotted lines indicate confidence intervals for the correlation (ii) excluding and including H-bonded materials, respectively. They are determined from data shown by Fig. 3 in Ref. [10] assuming confidence limits equaled 0.95 and using correlation coefficients equaled 0.92 (for H-bonded materials excluded) and 0.88 (for H-bonded materials included) reported in Ref. [10] for the correlation (ii). The inset shows scaling exponents $\gamma^{(corr)}$ collected in Table I and their confidence intervals which are obtained from the correlation (ii) at ambient and elevated pressure.

m_V were dependent on P, the scaling exponent γ should vary on pressure (see $m_V^{(corr)}$ and $\gamma^{(corr)}$ in Table I). Taking into account confidence intervals for $m_V^{(corr)}$, it turns out that the isochoric fragilities obtained from the correlation (i) at ambient and elevated pressures are different for three of the tested van der Waals liquids (PC, salol, PCB62) and all H-bonded systems (see the inset in Fig. 1). However, all the values of $\gamma^{(corr)}$ calculated from the correlation (ii) at pressure of 0.1 MPa and 0.6 GPa differ if we compare them remembering their confidence intervals (see the inset in Fig. 2). The simple analysis leads to the inconsistancy because the exponent γ commonly treated as a material constant should be independent of thermodynamical conditions. Moreover, the dependence of m_V on pressure is also controversial. As the isochoric fragility is calculated at constant density, it can only provide us useful information about the thermal contribution to molecular dynamics. Thus, the isochoric fragility should be rather independent of pressure. It can be illustrated using PDF data which leads to m_V=39.44 at 0.1 MPa and m_V=39.43 at 0.2 GPa. The results are obtained from Eq. (2a) using the published values [17] of $(1+\alpha_P/|\alpha_\tau|)^{-1}=E_V/H_P$ equaling 0.555 and 0.588 at ambient and evaluated pressure, respectively, as well as m_P=71 at 0.1 MPa [16] and m_P=67 at 0.2 GPa [4]. To sum up, since $m_P(P)\neq$const and $m_V(P)$=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. In the context of the above discussion, correlation (ii) seems to be universal, because if $m_V(P)$=const, then γ is also pressure independent. However, it is worth noticing that correlation (ii) should not be applied for H-bonded systems because, in their case, the exponents $\gamma^{(corr)}$ are distinctly not in accordance with the experimental values γ, even at ambient pressure (see Table I and Fig. 2, especially data for glycerol).

Strongly hydrogen-bonded materials, such as glycerol, sorbitol, propylene glycol (PG), dipropylene glycol (DPG), and tripropylene glycol (TPG), exhibit the opposite pattern of behavior for the pressure dependence of m_P as it has been established in the case of van der Waals liquids. The pressure coefficient of fragility dm/dP in the low pressure limit, which is a quantitative indicator of the monotonicity type of the dependence $m_P(P)$ [16], is positive for H-bonded materials unlike van der Waals liquids (see Table I). Magnitudes of m_P for the H-bonded systems increase on elevating pressure in the intermediate pressure range [18–20]. This fact is usually explained by a decrease of hydrogen bonding with increasing P and T [19,21]. Such behavior is an example of the significant influence of H-bonding on molecular dynamics and relaxation phenomena and reflects specific dynamics determined by temporary H-bonded networks with inter- and intramolecular links [22]. It would be a great achievement if one could describe properties of materials so different in their structures, such as van der Waals and H-bonded liquids, using correlations (i) and (ii) with the same parameters in any thermodynamic conditions. Then, it would be possible to

TABLE I. Results of the test of the correlations (i) and (ii) for van der Waals and H-bonded glass formers. The isochoric fragilities ${m_V}^{(corr)}$ are calculated from the correlation (i) using the isobaric fragilities m_P experimentally obtained at ambient and elevated pressure. The scaling exponents $\gamma^{(corr)}$ are derived from the correlation (ii) using the isochoric fragilities ${m_V}^{(corr)}$ previously found at 0.1 MPa and 0.6 GPa. The parameters of the correlations (i) and (ii) are taken from Ref. [10].

				$P=0.1$ MPa				$P=0.6$ GPa		
Material		γ exp.[a]	dm/dP at $P \to 0$ (GPa^{-1})[a]	m_P exp.[a]	m_V exp.[a]	${m_V}^{(corr)}$ corr. (i)	$\gamma^{(corr)}$ corr. (ii)	m_P exp.[b]	${m_V}^{(corr)}$ corr. (i)	$\gamma^{(corr)}$ corr. (ii)
van der Waals liquids	PC	3.7 4.2[c]	−18	81	57	52.4	3.10	73.2	43.2	3.99
	PDE	4.5	−30	71	39	40.5	4.32	65.4	33.8	5.37
	KDE	4.5	−17	64	34	32.1	5.71	57.4	24.3	7.89
	Salol	5.2	−11	68	36	36.9	4.84	57.2	24.1	7.96
	BMMPC	8.5	−23	58	25	25.0	7.64	51	16.7	11.98
	PCB62	8.5	−45	59	23	26.2	7.24	45	9.6	21.51
H-bonded liquids	Glycerol	1.8 1.4[c]	+35	54[d]	38	20.2	9.68	69[d]	38.1	4.65
	Sorbitol	0.13	—	128	112	108.3	0.96	—	—	—
	DPG	—	+59[e]	—	60[e]	27.4	6.88	92[e]	65.5	2.27
	TPG	—	+53[e]	70[e]	—	39.3	4.48	88[e]	60.7	2.53

[a] Reference [16].

[b] Reference [4].

[c] Reference [6].

[d] Reference [18].

[e] Reference [19]. The pressure coefficients of fragility dm/dP at $P \to 0$ are obtained on the basis of the inset in Fig. 4 *ibid.*

determine m_V and γ based on experimentally found values of m_P for any material at any P, V, and T. However, H-bonded systems do not seem to satisfy the correlations even at atmospheric pressure. It is clearly seen for glycerol (Table I, Figs. 1 and 2). For this material at ambient pressure, the isochoric fragility $m_V^{(corr)}$ calculated from correlation (i) is about 88% less than the one obtained experimentally [5,16], whereas the scaling exponent $\gamma^{(corr)}$, derived from the correlation (ii) with $m_V^{(corr)}$, is about 5.5 times larger than γ found [2] from fitting experimental data to Eq. (1). Moreover, one can observe that many points shown in the master plot for glycerol [6] diverge from one curve which could be treated as a master curve by means of Eq. (1). Somewhat different results are obtained for sorbitol at 0.1 MPa (see Table I). In this case the isochoric fragility $m_V^{(corr)}$ calculated from correlation (i) well corresponds with the experimental value [16]. However, the exponent $\gamma^{(corr)}$ followed from correlation (ii) with $m_V^{(corr)}$ is even 9.8 times larger than that obtained from the scaling procedure [3,16]. Similar calculations for glycerol, DPG, and TPG at 0.6 GPa lead to the problems analogous to those that appear for van der Waals glass formers. The isochoric fragilities $m_V^{(corr)}$ obtained from the correlation (i) also change on pressure due to changing $m_P(P)$. However, $m_V^{(corr)}$ increases with increasing pressure in the case of H-bonded systems (see Table I and the inset in Fig. 1). Consequently, we obtain the inconsistency that the scaling exponent $\gamma^{(corr)}$ derived from the correlation (ii) with $m_V^{(corr)}$ is strongly dependent on P (see the inset in Fig. 2). This result is again at odds with the statement that γ should be constant. However, in the case of H-bonded systems, 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

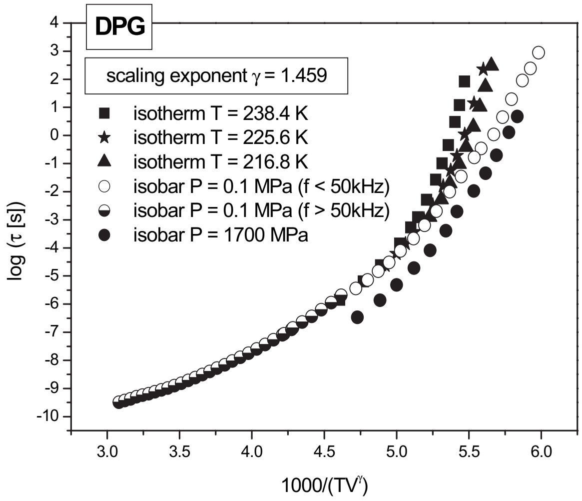

FIG. 3. Dielectric relaxation time for DPG vs $T^{-1}V^{-\gamma}$. Isothermal (■, ▲) and atmospheric isobaric (○) data are taken from Fig. 8 in Ref. [19]. Our isobaric data [20] obtained at $P=1.7$ GPa, as well as at higher frequency and at ambient pressure, are denoted by closed (●) and half-closed circles, respectively. The scaling exponent γ for DPG is calculated by means of Eqs. (2a) and (2b), as well as by the equation $(1+\alpha_P/|\alpha_\tau|)^{-1}=E_V/H_P$, using data for $\tau=0.01$ s and $P=0.1$ MPa collected in Ref. [19] (in Table I and in the inset in Fig. 6).

T, because the thermodynamic conditions strongly affect the degree of H bonds. Nevertheless, the mentioned dubious correspondence between the results of correlations (i) and (ii), as well as the experimental values of m_V and γ even at 0.1 MPa, demands us to seriously consider excluding some H-bonded systems from the correlations. As an illustration of problems with thermodynamic scaling in the case of H-bonded materials we show in Fig. 3 that dielectric data for DPG cannot be scaled. This means that dielectric isothermal and isobaric data for DPG taken from Refs. [19,20] cannot be plotted on one master curve, $\log_{10}\tau(T^{-1}V^{-\gamma})$. The scaling exponent, $\gamma=1.459$, is calculated by means of Eqs. (2a) and (2b), as well as by the equation $(1+\alpha_P/|\alpha_\tau|)^{-1}=E_V/H_P$, using data for DPG also published in Ref. [19]. In order to evaluate volume the Tait equation with its parameters reported in Ref. [19] is applied to our isobaric data [20] obtained at $P=1.7$ GPa, as well as at higher frequency and at ambient pressure [23].

Finally, it is worth mentioning that another correlation concerning the fragility loses its universality under elevated pressure. More than ten years ago, Böhmer *et al.* [24] proposed the rather rough correlation between the isobaric fragility m_P and the stretching exponent β_{KWW} of the Kohlrausch-Willams-Watts (KWW) function [25] using experimental data obtained at ambient pressure. Its form, $m_P=250\pm30-320\beta_{KWW}$, suggests that the parameter β_{KWW} should change with varying m_P, which is observed under elevated pressure as has been already mentioned herein. However, Ngai *et al.* [26] have recently shown for several glass formers that the parameter β_{KWW}, which characterizes the breadth and asymmetry of the structural relaxation peak, does not change with elevating pressure. The interesting phenomenon is an additional argument for reanalyzing correlations which aspire to be universal in any pressure, volume, and temperature conditions such as those found in the context of the thermodynamic scaling.

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