Fragility and basic process energies in vitrifying systems

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The concept of ‘fragility’ constitutes a central point of the glass transition science serving as the ‘universal’ metric linking previtreous dynamics of qualitatively distinct systems. Finding the fundamental meaning of fragility is the ‘condicio sine qua’ for reaching the long expected conceptual breakthrough in this domain. This report shows that fragility is determined by the ratio between two fundamental process energies, viz. the activation enthalpy and activation energy. The reasoning, avoiding any underlying physical model, is supported by the experimental evidence ranging from low molecular weight liquids and polymers to plastic crystals and liquid crystals. All these lead to the new general scaling plot for dynamics of arbitrary glass formers. The limited adequacy of broadly used so far semi-empirical relationships between fragility and the activation energy is shown. Results presented remain valid for an arbitrary complex system and collective phenomena if their dynamics is described by the general super-Arrhenius relation.

Glass transition constitutes one of grand challenges of condensed and soft matter physics as well as modern materials science 1-4, where a long-expected fundamental breakthrough could lead to innovative implementations ranging from silicate glasses 5 and plastics 6 to pharmaceuticals 7 and foods 8. The ultimate progress in this area is also important for biotechnological 9, geophysical 10, metallurgical 11 and electronic devices 12 implementations. Notable is the fact that glass transition physics is considered as one of key references for collective phenomena science, aimed to discover properties emerging from complex correlations 13.

Of particular interest of the glass transition research is the identification of universal features in the previtrous dynamic regime shared amongst a surprising variety of systems including low molecular weight liquids, polymers, liquids crystals, plastic crystals, colloids, metallic alloys, silicates, spin glasses, etc 2-5. A key metric linking so distinct systems with highly SA behaviors, with close-to-Arrhenius behavior (Tg)~m(T) for structural (primary) relaxation time and Tg is the glass temperature 14,15. This was possible due to the empirical normalization assumption for the glass transition temperature η(Tg) = 1015 Poise and η(Tg) = 100 s. Subsequently, a metric describing the slope for T → Tg called ‘fragility’, was proposed 14,15:

\[ m = m(T_g) = \frac{d \log_{10} \eta(T)}{d(T_g/T)} \]  

or

\[ m = m(T_g) = \frac{d \log_{10} \eta(T)}{d(T_g/T)} \]  

The fragility index m describes the degree of shifting from the basic Arrhenius dynamics to the super-Arrhenius (SA) one, described by the general form 2,15:

\[ \tau(T) = \tau_0 \exp \left( \frac{\Delta E_a(T)}{RT} \right) \quad \text{or} \quad \eta(T) = \eta_0 \exp \left( \frac{\Delta E_a(T)}{RT} \right) \]  

where T > Tg, R denotes the gas constant and ΔEa(T) the apparent activation energy. The basic Arrhenius dependence is restored for ΔEa(T) = Ea = const.

There are two general types of glass transition defined by the fragility metric: (i) ‘fragile’ systems with highly SA dynamics (m > 50) and (ii) ‘strong’ ones, with close-to-Arrhenius behavior (m < 30). 14,15. The basic Arrhenius behavior \( \tau(T) = \tau_0 \exp(E_a/RT) \) is associated with the minimal value of the fragility index and most often related to m = log10(τ(T = Tg)) - log10 τ0 = 2 + 14 = 16, i.e. assuming for the prefactor τ0 = 10^{-14} s in the SA eq. (2). 2,15. Notwithstanding, for silicate liquids extremely strong SA behavior with a minimal m = 14.93 was found 16.
Experimental estimations of the prefactor in the SA equation ranges from $\sim 10^{-16}$ s to even $\sim 10^{-18}$ s, what indicates on the system-dependent minimal fragility.

Qualitative mapping of the previtrous increase of relaxation times or viscosity onto a single chart has led to the concept of fragility, becoming a focal point for research in glass transition physics$^{5,23}$. The most important appeared as the link between two basic properties, viz. fragility and the activation energy$^{7,2,16-20}$. One may claim that the ultimate explanation of this problem is the "condicio sine qua" for reaching the conceptual breakthrough in glass transition physics$^{25}$. Surprisingly, despite decades of studies the situation is puzzling.

The first and broadly implemented up to now dependence$^{20-26}$ was proposed by Boehmer et al.$^{15}$ in 1993:

$$\Delta E_a(T_g) = \Delta E_a(T/T_g \to 1) = RT_g m \ln 10$$

(3)

In 2004, Novikov and Sokolov$^{27}$ proposed yet another relation, supported by experimental evidence for a set of glass forming liquids$^{27,28}$:

$$\Delta E_a(T_g/T \to 0) = (19.2) T_g \ln 10 / m$$

(4)

This report presents the critical discussion of eqs. (3) and (4) and shows that their validity is casual. Subsequently, it presents the lacking so far fundamental link between fragility and fundamental process energies, viz. the activation energy and the activation enthalpy. The new, ‘ultimate’, scaling relation linking fragility and the activation energy has been also derived. Analytic results are supported by the clear experimental evidence for a broad range of glass formers.

Results

The new insight into fragility of glass formers. In Refs. 29, 30 the new approach for the insight dynamics of the previtrous domain, based solely on the SA eq. (2) and the metric describing relative changes of the apparent activation energy was introduced:

$$I_{DO}(T) = - d \Delta E_a(T)/dT / d \Delta E_a(T) = - d \ln \Delta E_a(T) / d \ln T$$

(5)

The analysis in Refs. 29, 30 was possible due to the innovative way of determining $\Delta E_a(T)$, which avoids the biasing impact of generally unknown prefactor $\tau_0$ in the SA eq. (2). This model-free approach leads to a set of notable findings including the limited fundamental adequacy of the Vogel-Fulcher-Tamman (VFT)$^{31-33}$ equation, identifying the role of local symmetry in glass formation and showing the ultimate way of “dynamic” estimation of the ideal glass transition temperature$^{39,30}$.

Linking the SA eq. (2) and eq. (5) for the apparent activation energy temperature index one obtains:

$$\Delta H_a'(T) = \frac{\Delta H_a(T)}{R} = \frac{\delta \ln \tau(T)}{\delta (T/T)}$$

$$[\frac{1}{T^2} \Delta E_a(T)] = \Delta H_a(T) [1 - I_{DO}(T)]$$

(6)

where the identity $d(1/T) = -(1/t) dT / d(1/T) = -(d \ln T) / d(1/T)$ was used, $\Delta H_a(T)$ denotes the apparent enthalpy (see also Ref. 17 and Suppl. Info of Refs. 29, 30 where clear derivations of the relationship between $\Delta E_a(T)$, $\Delta H_a(T)$ and $d \ln T / d(1/T)$ are given), $\Delta E_a(T) = \Delta E_a(T) / R$.

The above dependence directly yields:

$$I_{DO}(T) = \frac{\Delta H_a(T)}{\Delta E_a(T)} - 1$$

(7)

Figure 1 shows that eq. (7) can serve as the base for the new “universal scaling plot” for the previtrous dynamics of arbitrary glass former. It includes representatives from LMW, P, ODIC and LC categories$^{29,30,34-39}$. Notable is the correlation with the classical ‘Arrhenius’ plot$^{5,14,15}$, presented in the inset for the same systems. For both plots the increase of curvature indicates the rise of fragility. However, in the main plot fragility is directly determined by the ratio of fundamental process energies, namely:

$$I_{DO}(T) = \frac{T_g}{T} \frac{d \ln \Delta E_a(T)}{d \Delta E_a(T)}$$

(8)

which lead to:

$$M = I_{DO}(T_g) = \frac{d \ln \Delta E_a(T)}{d \Delta E_a(T)} = \frac{\Delta H_a(T_g)}{\Delta E_a(T_g)} - 1$$

(9)

The onset of the Arrhenius behavior is associated with the negligible curvature and almost horizontal behavior for $\Delta H_a(T)/\Delta E_a(T) \ll 1$ in Fig. 1.

The classical fragility index $m$ (eq. (1)) is still explained as the ‘formal’ parameter, namely the slope at the ‘Arrhenius’ plot$^{5,14,15}$. The new fragility parameter $M = I_{DO}(T_g)$ gives directly value between two basic process energies, which are then key fundamental features determining the value of fragility. Using eqs. (1), (2) and (9) one obtains the link between the ‘classical’ ($m$) and new ($M$) fragility metrics:

$$m = C(1 + M) = C(1 + I_{DO}(T_g)) = C \frac{\Delta H_a(T_g)}{\Delta E_a(T_g)}$$

(10)

where the constant $C = 2 - \log_{10}(\tau_0) = 13-18$.

The relationship between $m$ and $I_{DO}(T_g)$ was indicated earlier by Heckscher et al.$^{40}$, but without an explanation of the physical meaning of $I_{DO}(T_g)$.

The experimental confirmation of the behavior predicted by eq. (10) is given in Figure 2. It is notable that eq. (10), showing also the link of $m$ to basic process energies, indicates also the uncertainty introduced by the prefactor $\tau_0$ or $\eta_0$ in SA eq. (2). The summary of characteristics for aforementioned experimental systems is given in Table 1.

However, the most fundamental eqs. (1) and (2) directly indicate that the increasing SA behavior is associated with the rising nonlinearity at the “Arrhenius-type” plot $\ln(\Delta E_a(T))$ vs. $1/T$. Fig. 3 presents such plot, revealing the lack of a correlation between the increasing curvature of the apparent activation energy, coupled to rising fragility $m$, and the value of $\Delta E_a(T)$. This is in clear disagreement with mentioned above basic prediction (eq. (3)). Moreover, the simply linearization based on eqs. (1) and (2) yields $\ln(\Delta E_a(T)/T_g) = \ln[m + cte/\Delta E_a(T_g)]$, i.e. the linear function with the intercept at $cte = \ln[R T_g \ln 10] > 0$ and the directional factor $b = 1$. Such prediction is anti-correlated with experimental data, as shown in the inset in Fig. 3 via the dashed line. Consequently, the used so far basic link between the activation energy and fragility $\Delta E_a(T_g) = RT_g m \ln 10$, (i.e. (eq. (3))$^{14,16,20-26}$, is inherently invalid.

However, the simple analysis based solely on general eqs. (1) and (2) and (9), derived above yields (see also Methods section):

$$\Delta E_a(T_g) = RT_g m \ln 10 - \left( \frac{\partial \Delta E_a(T)}{\partial (T_g/T)} \right)_{T=T_g}$$

(11)

Figure 4 shows that the implementation of eq. (11) orders “chaotically scattered” curves in the main part of Fig. 3. It also leads to the superior agreement with experimental data given the inset in Fig. 3 (the solid line). Consequently, eq. (11) can be considered as the new ultimate link between the activation energy and fragility, valid for an arbitrary glass former.
Novikov and Sokolov proposed yet another relation linking fragility (determined for $T_g / T \to 1$) with the activation energy but this time taken for $T_r / T \to 0$, viz. eq. (4). For explaining its meaning, let’s recall that in the low temperature domain ($T_g / T \to 1$) the increase of curvature and the slope in the ‘Angell’ plot is linked to increasing value of $m$. For the same plot, $\log_{10} \eta(T)$ or $\log_{10} \tau(T)$ vs. $T_g / T$, in the high temperature domain the decreasing slope is related to increasing value of $m$. This behavior is illustrated in Figure 5, showing that Novikov and Sokolov relation $\Delta E_a(T_g / T \to 0) \sim 1 / m$ (eq. (4)) results from the construction of the ‘Angell’ plot. The underlying assumption of eq. (4) is also the “universal” value of the viscosity ($\log_{10} \eta_0 = -4$) or for relaxation time $\log_{10} \tau_0 = -14$ for $T_g / T \to 0$. This border values are considered as hypothetical universal values of the prefactor in the SA eqs. (1).

However, the existence of such universal values of prefactors can be questioned, particularly when taking into account different categories of glass formers, as discussed above. All these indicate on the necessity of a supplementary analysis, related to: (i) the activation energy determined without the biasing impact of the prefactor and (ii) the impact of the qualitative differences between dynamic the high- and low- temperatures domains. The latter is particularly important, because eq. (4) suggests direct causal link between different dynamic domains.

Following the above discussion, as well as the evidence from Refs. 2, 29, 30, one can indicate following basic features of the ultraslowing/ultraviscous domain:

- There are no glass forming systems in the ultraviscous/ultraslowing domain where $\Delta E_a(T)$ decreases on cooling, i.e. $\forall T_r < T < T_v$, $\partial \Delta E_a(T) / \partial (1 / T) \geq 0$ and $I_{DO}(T) \geq 0$.
- For extremely strong glass formers $\Delta E_a(T) \sim \Delta H_a(T)$ for the whole low temperature dynamic domain. In the case of the Arrhenius behavior $\Delta E_a(T) = \Delta H_a(T) = const$.
- In the ultraviscous/ultraslowing domain always $\Delta H_a(T) > \Delta E_a(T)$ and in the vicinity of $T_g$ even $\Delta H_a(T) \gg \Delta E_a(T)$. This is particularly evident for fragile ultraslowing and/or ultraviscous systems.

**Discussion**

The fragility and the activation energy are the most fundamental characteristics of glass transition. One can expect that a conceptual progress in this challenging area of condensed matter physics needs the unequivocal relationship between these quantities. However, this basic problem appeared to be surprisingly difficult, viz. the title of the recent Ref. 42: “The fragility and other properties of glass-forming liquids: Two decades of puzzling correlations”.

The current report presents the first ever evidence of the unequivocal link between fragility and ratio of two basic process energies: the activation energy and the activation enthalpy in the low temperature ultraviscous/ultraslowing dynamic domain. It is worth recalling that the activation energy $\Delta E_a(T)$ is associated with the energy barrier necessary to boost a process, i.e. a transition state’s free energy (the energy barrier) minus the energy of substrate’s. This report shows the direct link of fragility to the ratio of these energies: $m = (2 - \log_{10} \tau_0) (\Delta H_a(T_g) / \Delta E_a(T_g))$, but affected by the uncertainty associated with the SA prefactor $\tau_0$ (or $\eta_0$). This biasing impact can be avoided for the
new fragility metric \( M = I_{DO}(T_g) = \Delta H_a(T_g)/\Delta E_a(T_g) - 1 \), ranging from \( M = 0 \) (the basic Arrhenius case) to \( M > 10 \) for strongly SA dynamics. The activation enthalpy can be easily calculated via \( \Delta H_a(T) = \Delta H_a(T) + \Delta R(T/T_g - 1) \) or \( \Delta H_a = d \ln \eta(T)/d(1/T) \) and the activation energy via the recently proposed model free route procedure (see Methods and Refs. 29, 30). This report shows that in the ultraviscous/ultraslowing domain always \( \Delta H_a(T) > \Delta E_a(T) \) and in the immediate vicinity of \( T_g \) even \( \Delta H_a(T) \gg \Delta E_a(T) \). We emphasize this issue, since in a number of research reports the erroneous assumption that \( \Delta E_a(T) = d \ln \tau(T)/d(1/T) \) near the glass transition has been used.\(^{20-23,45-49}\)

One of the most attracting questions regarding fragility is its maximal value. In Ref. 50 values \( m \approx 175 \) was indicated as the maximal possible fragility, what is related to \( M \approx 10 \). However, earlier \( m \approx 214 \) was noted as the indicator of the most SA dynamics.\(^{51}\) Basing on this report, recalling the basic Adam-Gibbs (AG) theory\(^ {2,52} \) and Refs. 29, 30 the following general dependence for the apparent activation energy temperature index can be obtained (see Methods section):

\[
I_{DO}(T) = \frac{nT_N}{T-T_N},
\]

\( I_{DO} \) is the glass transition temperature.

The latter dependence and eq. (9) yields:

\[
M = n \frac{T_N}{T_g - T_N} \quad \text{and} \quad m = C \left( 1 + n \frac{T_N}{T_g - T_N} \right)
\]

For example, for glass formers with rod-like molecules and the clear uniaxial, orientational symmetry \( n = 1.6 \) and \( T_g - T_N \approx 10 \) with \( T_N \approx 300 \) K (see Suppl. Info to Ref. 30) one obtains \( m \approx 280! \)

Following the given report and Refs. 29, 30 one can postulate that the transformation of \( \tau(T) \) or \( \eta(T) \) experimental data to \( I_{DO}(T) \) representation can yield all basic characteristics of previtreous dynamics, basing solely on inherently unambiguous linear regression fit, namely: (i) the local symmetry related parameter \( n = -1/I_{DO}^{\gamma}(0) \), (ii) the extrapolated singular temperature for which \( I_{DO}^{\gamma}(T_N) = 0 \) and (iii) the fragility metric \( M = I_{DO}(T_g) \), linked to basic process energies. Knowing \( (T_N, M, n) \) (see Fig. 6 in Methods section) and the fragility \( m \) (from the “Angell” plot) the unambiguous estimation of \( \tau_0 \) or \( \eta_0 \) prefactors is also possible.

One of still mysterious features of the glass transition are different distances between the glass temperature \( (T_g) \) and the extrapolated Kauzmann temperature \( (T_K) \) in various glass formers\(^ {2,53} \). Following the finding the \( T_N = T_K \) (see Ref. 30 and Methods section) and eq.

### Table 1

| Sym. | System                  | Full name                        | \( T_g/K \) | \( T_N/K \) | \( n \)  | \( m \)  | \( M \)  | \( R/K \) |
|------|------------------------|----------------------------------|------------|------------|--------|--------|--------|--------|
| O    | Cyanoadamantane (ODIC) | CNa  |
| C    | Cycloheptanol(57%) + Cyclooctanol(43%) (ODIC) | C8C7 |
| C    | Cyanocyclohexane (ODIC) | CNe |
| E    | Ethanol (LMW) | Ethn |
| O    | Isooctylcyanobiphenyl (LC) | OCBO  |
| C    | Propylene carbonate (LMW) | PC   |

The figure indicates the lack of correlation between increasing curvature, coupled to fragility, and the value of \( \Delta E_a(T_g) \). The clear disagreement with eq. (3) is stressed by the inset: the blue, dashed line is related to eq. (3) and the solid, black line is based on the MFR.

Figure 3 | Degree of nonlinearity at “Arrhenius-type” plotted as \( \ln(\Delta E_a(T_g))/T_g \) vs. \( T_g/T \) for representative glass formers. The figure indicates the lack of correlation between increasing curvature, coupled to fragility, and the value of \( \Delta E_a(T_g) \). The clear disagreement with eq. (3) is stressed by the inset: the blue, dashed line is related to eq. (3) and the solid, black line is based on the MFR.

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The apparent activation energy is obtained by MFR procedure (see Methods) which is rescaled at $T_g$ using eq. (11). The figure shows the correlation between increasing curvature, indicating the rise of fragility, and $\Delta E_a(T_g)$. For basic data see also Table 1.

(13) one obtains $M/n = T_s/T_g - T_N = M/n$, i.e. the relative distance between $T_s = T_N$ and $T_g$ depends solely on the fragility ($M$) and symmetry related ($n$). It is notable that eq. (13) makes possible also unequivocal calculation the $T_0$ for the SA eq. (2), avoiding any "ersatz equations", like the VFT one used so far.

Worth noting is the relationship of the new fragility parameter $M$ to the one introduced by Doremus[5], who applied the empirical finding that at high temperature (HT) the activation energy low ($\Delta E_a^HT$, originally denoted as $Q_L$ is low) whereas at low temperatures prior to the vitrification its value is high ($Q_D$, $\Delta E_a^HT$). This lead to the Doremus fragility metric $R_D = Q_D/Q_L = \Delta E_a^HT/\Delta E_a^HT$ with $R_D < 2$ for "strong" glass formers and $R_D > 2$ for "fragile" ones$^{5,6}$. In the Doremus model $Q_H = H_D + H_m$, where $H_D$ is associated with enthalpy of formation of broken bonds and $H_m$ is responsible for motions. At high temperature $H_m$ dominates and $Q_L = H_m$. Such picture results from the fact that Doremus introduced the model for ultravisous silica, but its extension to other glass formers can be explained by the formations of bond-ordering local structures or heterogeneities. This led Doremus to the double-exponential function for description of the viscous flow, at least in silicates$^{6,7}$. This way of determining $\eta(T)$ was only recently introduced in Refs. 29, 30. Previously, the apparent activation energy was calculated from the SA eq.(2) as

$$\Delta E_a(T) = \Delta E_a(T_0) = \frac{d \ln \eta(T)}{d \ln T} \approx \frac{\Delta E_a(T_0)}{\ln(T/T_0)}$$

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where the apparent activation enthalpy is given by $\Delta H_a(T) = \Delta H_a/R = d \ln \eta(T)/d(1/T)$.

The analysis of experimental data and the model-free route (MFR) method. The "model-free" route procedure introduced in Refs. 29, 30 is a novel approach for getting insight into previtreous dynamics based on the transformation of basic structural relaxation time ($\tau(T)$) or viscosity ($\eta(T)$) experimental data to apparent activation energy temperature index form, the magnitude first proposed for glass formers by Dyre and Olsen (DO)$^{8}$ as:

$\ln(\tau(T)) = \ln(\tau(T_0)) - \frac{\Delta E_a(T_0)}{R} \frac{1}{T} + \ln C_1$,

where $\tau(T)$ is the singular temperature estimated via $\ln(\tau(T)) = \ln(\tau(T_0)) - \frac{\Delta E_a(T_0)}{R} \frac{1}{T}$, where the power exponent is determined as $n = \frac{1}{\tau(T_0)/\tau(T_{15})}$, and then it was inherently biased by the generally unknown estimation of $\tau_0$ prefactor$^7$. In practice, a "universal" value of $\tau_0 = 10^{-14} \text{s}$ was most commonly assumed$^7$. An inherent advantage of the MFR approach for determining $\Delta E_a(T)$ and $\Delta H_a(T)$ includes also the application of a numerical filtering procedure based on Savitzky-Golay principle$^{9,10}$.

In Refs. 29, 30 the MFR have been implemented for a set of 55 glass forming systems, ranging from low molecular weight liquids (LMW) and polymers (P) to liquid crystal (LC), plastic crystal (ODIC) and spin glasses (SGL), in the previtreous domain. The analysis revealed a surprisingly simple pattern for the previtreous dynamics: $1/\tau_0(T) = aT + b$, with $a \neq 0$ and $b \neq 0$ for all mentioned data sets. This led to the derivation of the new generalization of the so-called $\tau_0$ prefactor$^7$. Only in this case the application of the popular Vogel-Fulcher-Tammann (VFT)$^7$ equation is suitable$^{10}$. Consequently, the fundamental justification of the VFT relation is limited to a small group of glass formers and otherwise (i.e. for $n \neq 1$) it can be considered solely as an effecting fitting tool.

The example of analysis employing the MFR analysis, based on transformed $\tau(T)$ experimental data in supercooled liquid crystalline 4-octyloxycyanobiphenyl (8OCB), is shown in Fig. 6. The way of determining the basic parameters is indicated.

Values of primary relaxation times $\tau(T)$ were determined as the reciprocal of the peak frequency of $\varepsilon''(\omega)$ loss curve, obtained from broad band dielectric spectroscopy measurement (see Refs. 29, 30).
Tn contribution in the anomalous behavior of the activation entropy temperature index.

Figure 6 | The temperature scaling behavior of the reciprocal of the crossover temperature

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**Author contributions**

J.C.M.G., S.J.R. and A.D.R. wrote the main manuscript, J.C.M.G. prepared figures, S.z.S. worked on data analysis, J.C.M. finally shaped the form of the manuscript. Authors’ related experimental results are associated with measurements carried out J.C.M.G., S.J.R. and A.D.R. New conceptions proposed in the paper are proposed mainly by J.C.M.G. and S.J.R. but finally influenced by A.D.R. and J.C.M.

**Additional information**

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