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Divergent dynamics and the Kauzmann temperature in glass forming systems

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In the last decade the challenging analysis of previtreous behavior of relaxation time ($\tau(T)$) in ultraviscous low molecular weight liquids led to the conceptual shift of the glass transition physics toward theories not predicting a “finite-temperature” divergence. This “breakthrough” experimental finding was strengthened by the discovery that “dynamic” (i.e. from $\tau(T)$ fitting) and “thermodynamic” estimations of the “ideal glass” (Kauzmann) temperature do not match, what in fact questioned its existence. In this report, due to the novel way of analysis based on the transformation of $\tau(T)$ experimental data to the activation energy temperature index form, the clear prevalence of the “finite-temperature” divergence is proved. The obtained “dynamic” singular temperatures clearly coincide with “thermodynamic” estimations of the Kauzmann temperature, thus solving also the second mystery. The comprehensive picture was obtained due to the analysis of 55 experimental data-sets, ranging from low molecular weight liquids and polymers to liquid crystal and plastic crystals.

The glass transition phenomenon is one of key challenges of the modern material science, condensed matter physics and soft matter physics^{1–5}. For the latter it constitutes even the general reference for dynamics in the variety of systems within this category⁵. Glass transition physics is also recognized as one of key references for the general science of collective phenomena, aimed to discover properties emerging from complex correlations⁶. The practical significance of the glass transition extends from glass⁷, petroleum⁸, plastics⁹, pharmaceutical¹⁰ and food industries¹¹ to geophysics¹² and issues related to environmental protection⁹.

However, in the last decade experimental results appeared that significantly disrupted much of the established wisdoms in glass transition physics. First, Hecksher et al.¹³ presented analysis of the evolution of the primary relaxation time in 42 supercooled low molecular weight glass forming liquids and noted a clear preference for parameterization without a “finite-temperature” divergence. This coincided with the earlier discovery of Tanaka¹⁴ that “dynamic” and “thermodynamic” estimates of the ideal glass Kauzmann temperature¹⁵, located below the glass temperature T_g , differ qualitatively.

These findings became a kind of “experimental Rosetta Stone”, inspiring qualitatively new theoretical searches in the glass transition physics^{3,4,6,16–22}.

In this report, 42 experimental data-sets from the paper by Hecksher et al.¹³ are re-analysed. Due to the implementation of the novel, “model free” analysis it is shown that for each set of these data the dynamics is associated with the finite temperature divergence, contradicting the key conclusion of ref. 13. Subsequently, the analysis is extended for 13 data-sets covering also liquid crystals, plastic crystals, spin glass-like systems, and polymers. Basing on results obtained it is indicated that the proper strategy for the ultimate insight into dynamics of glass forming systems may be comprehensive studies of different categories of glass formers.

The new “model free” approach, explores the reciprocal of the Dyre-Olsen (DO) activation energy temperature index $1/I_{DO} = [-d\ln\Delta E_a/d\ln T]^{-1}$, where $\Delta E_a(T)$ defines the temperature-dependent apparent activation energy²³. A preference for parameterization with the finite-temperature divergence is clearly shown and the novel metric characterizing arbitrary glass former $n = -1/I_{DO}^{-1}(T=0)$ is proposed^{23,24}. Finally, the novel way of determining the ideal glass Kauzmann temperature (T_K) which solves the fundamental puzzle of Tanaka¹⁴ is proposed.

As mentioned above, the basic artifact constituting the check point for theoretical models of the glass transition is the optimal parameterization of the evolution of primary relaxation time $\tau(T)$ or viscosity $\eta(T)$ upon approach-



ing T_g , appeared to be elusive. The most basic feature of previtrification processes is the dramatic increase of the apparent activation energy what gives rise to the general super-Arrhenius equation (SA)^{3,4,6}:

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta E_a(T)}{RT}\right) \quad (1)$$

where R denotes the gas constant. Parallel equations are valid for viscosity, diffusion coefficient, and resistivity^{3,25}. For $\Delta E_a(T) = \Delta E_a = \text{const}$ one obtains the simple Arrhenius relation.

This research report focuses on $\tau(T)$ behavior, which can be estimated with particularly high resolution and reliability via modern broad band dielectric spectroscopy from coordinates of primary relaxation loss curves peaks³. However, conclusions presented below extend also for the other aforementioned dynamic properties. Unfortunately, the general SA eq. (1) is not directly applicable, due to the unknown form of $\Delta E_a(T)$ evolution. Consequently, alternative equations have been used. The most dominant is the Vogel-Fulcher-Tammann (VFT) dependence^{3,26–28}:

$$\tau(T) = \tau_0 \exp\left(\frac{D_T T_0}{T - T_0}\right) \quad (2)$$

where D_T denotes the fragility strength coefficient. Experiments for organic molecular glass forming liquid glass yield most often $T_0 \approx T_g - 30\text{K}$.

The coefficient D_T is considered as one of the most important metrics of fragility, which orders SA dynamics of molecularly different glass forming systems^{3,29,30}. Assuming a “universal value” for the prefactor $\tau_0 = 10^{-14}$ s and $\tau(T_g) = 100$ s one obtains relation $D_T \approx 590/(m - 16)$, where $m = [d \log_{10} \tau(T)/d(T_g/T)]_{T=T_g} = [d \log_{10} \eta(T)/d(T_g/T)]_{T=T_g}$ is the basic fragility metric^{29,30}.

The unique position of the VFT equation is also associated with the fact that it became a key checkpoint for basic glass transition theories/models^{3,4,6,14,21}. The most notable is Adam-Gibbs theory^{3,31}, in which the ultraviscous liquid consists of a number of independently relaxing regions, composed of a group of atoms or molecules that can rearrange cooperatively. On cooling toward T_g the configurational entropy of the system diminishes as the size of the cooperatively rearranging regions (CRR) grows progressively larger, leading to an increase in the structural relaxation time, expressed via^{3,31}:

$$\tau(T) = \tau_0 \exp\left(\frac{A \Delta \mu}{TS_C}\right) \quad (3)$$

where $\Delta \mu$ defines the free energy barrier between CRRs, S_C is the configurational entropy related to the difference between the entropy of the metastable supercooled liquid state and the corresponding equilibrium crystal, and A is a constant. Combining eqs. (1) and (3) one obtains: $\Delta E_a(T) \propto 1/S_C(T)$.

The AG eq. (3) can be transformed to the VFT form assuming $S_C = S_0(1 - T_K/T)$ and $T_0 = T_K$ ³¹. The latter denotes the extrapolated below T_g temperature for which entropies of the ultraviscous liquids and the “ground, stable” crystalline state matches^{3,6,31}. This “ideal glass transition temperature”, often recalled as the Kauzmann temperature (T_K)¹⁵, is recognized alternatively as one of the most fundamental or controversial properties of glass forming liquids^{3,4,6,21}. Basically, T_K is estimated from thermodynamic heat capacity studies, but the above discussion opened the route for the much more experimentally convenient estimations via the VFT equation^{3,4,6}. This formed the basis for research regarding the coincidence of the “thermodynamic” and “dynamic” estimations of T_K . The ultimate answer to this question is closely related to one of the most basic problems of glass transition physics, namely, if the vitrification is associated with a hidden phase transition well below the laboratory T_g ⁷. A milestone

result was reported in 2003 by Tanaka¹⁴, who compiled experimental data for 18 ultraviscous liquids and concluded that: “... T_K/T_0 systematically increases from unity with a decrease in the fragility (i.e.: D_T), contrary to the common belief...”. In subsequent years this result had been reduced to the generalized message¹³: “...Tanaka presented a compilation of data showing that $T_0 = T_K$ is not confirmed by experiment...” and became a significant source of questioning even the experimental existence of T_K . In 2008 Hecksher et al.¹³ carried out fitting comparison of $\tau(T)$ data for 42 glass forming low molecular weight organic liquids in the ultraviscous domain. They showed notable prevalence of parameterization via two formal functions (FF) without the “finite temperature” “divergence” over the VFT parameterization. In their conclusions, Hecksher et al.¹³ stated: “The observation that data are well fitted by the VFT equation was used to justify a search for models with a dynamic divergence. Our findings indicate that this is probably not a fruitful route. Thus, with Occam’s razor in mind — it is vain to do with more what can be done with fewer — we suggest that in the search for the correct theory for ultraviscous liquid dynamics, theories not predicting a dynamic divergence of the VFT form should be focused on.”

Refs. 13,14 became very influential references for searching new paths in glass transition physics and stimulating the search of new equations portraying $\tau(T)$ or $\eta(T)$ SA evolution without a finite temperature divergence. The possible lack of the finite temperature divergence below T_g and then also the non-existence of the Kauzmann temperature in “dynamic” $\tau(T)$ link or $\eta(T)$ studies significantly questioned also the hypothetical connection between the glass transition and phase transitions/critical phenomena physics^{4,16–20}.

The essential importance of problems discussed above, particularly Kauzmann temperature, has been clearly strengthened in the recent review⁴: “...It would be a major theoretical accomplishment to identify logically airtight tests that could establish whether the glass transition in a given system or model is caused by a dearth of entropy or by purely kinetic constraints. This would enable a currently lacking unambiguous distinction between correlations, such as are observed between kinetics and thermodynamics in many glass-forming systems, and causal relations...”.

The response to the above fundamental questions is the focus of the current report. First, the same 42 sets of data as used by Hecksher et al.¹³ for ultraviscous low molecular weight liquids (L), have been re-analyzed. The assembly of experimental results was supplemented by 13 sets of $\tau(T)$ data from the authors in ref. 23, covering also glass forming polymers (P), liquid crystals (LC), orientationally disordered crystals (ODICs, plastic crystals) and spin-glass-like systems (SGLs). It is notable that the main-stream discussion of “previtreous” dynamics focuses on (L) and (P) cases, and the rest of systems are often considered as separate issues in glass transition physics³. This is particularly notable for the SGLs case. As in ref. 13 the analysis was carried out in the low-temperature dynamic domain for $\tau(T_g) = 100\text{s} < \tau(T) < \tau(T_B) \approx 10^{-7}\text{s}$, where T_B denotes the dynamic crossover temperature. The up-to-date discussion related to the latter can be found in ref. 22.

In this report we show the existence of a new singular temperature $0 < T_N < T_g$ and the new, local symmetry related parameter n , characterizing arbitrary glass former and indicative for the finite-temperature divergent dynamics. All these lead to the explanation of the discrepancy between T_0 (VFT) and T_K (Kauzmann) temperatures noted by Tanaka¹⁴ and indicates a new dynamic and model-free way of analysis of dynamics in ultraviscous/ultraslowing glass forming systems.

Data analysis

Hecksher et al.¹³ indicated that a direct comparison of the fitting quality of experimental $\tau(T)$ data may not be a decisive route. They proposed to apply the activation energy temperature index, introduced earlier by Dyre and Olsen (DO)²⁴:



$$I_{DO}(T) = -\frac{d \ln \Delta E_a(T)}{d \ln T} \quad (4)$$

This can serve as the alternative metric of fragility, with a form recalling the Grueneisen parameter²³. However, there is a basic problem with determining $\Delta E_a(T)$ from $\tau(T)$ experimental data. The derivative procedure, sometimes used erroneously, yields an apparent activation enthalpy: $H'_a(T) = H_a/R = d \ln \tau(T)/d(1/T)$ instead of $\Delta E_a(T)$ ³³. So, the latter has to be calculated directly from eq. (1) via: $\Delta E'_a(T) = \Delta E_a/R = T \ln(\tau(T)/\tau_0)$, as it was done in in ref. 13. Unfortunately, this procedure requires prior knowledge of the prefactor τ_0 . Hecksher et al.¹³ assumed two universal values of $\tau_0 = (10^{-14}, 10^{-13})$ s for each of 42 tested ultraviscous liquids. Such values are often considered as “universal/averaged” prefactors, and have also some theoretical justification^{3,13,30}. Notwithstanding, in practice the analysis based on the VFT parameterization showed a broader range of $10^{-16} \text{ s} < \tau_0 < 10^{-10} \text{ s}$ ³³. The improper value of τ_0 assumed for a given system could therefore yield notable biasing in the evolution of $\Delta E_a(T)$.

In this report a novel procedure introduced recently is employed²³. It is based on the numerical solution of the differential equation $\partial \Delta E'_a / \partial (1/T) + \Delta E'_a / (1/T) = H'_a / (1/T)$ ²³, resulting directly from eq. (1), which avoids the requirement of knowing the prefactor in advance. The description of the employed procedure, avoiding the *a priori* knowledge of the prefactor τ_0 , is presented in the Supplementary Information.

We also employ the recent authors' finding²³ that the reciprocal of the DO index in the ultraviscous/ultraslowing domain follows a linear dependence for basic relations employed for $\tau(T)$ parameterization: VFT^{26–28}, Avramov-Baessler (AB)^{34,35}, Waterton-Mauro (WM, MYEGA)^{20,36} and the critical-like (Crit.)^{33,37}. The last one, obeying in LCs and ODICs, is particularly important for the current paper^{22,23,37}:

$$\tau(T) = \tau_c \left(\frac{T - T_c}{T_c} \right)^{-\phi} \quad (5)$$

where $T < T_c$, $T_c = T_g - (10 \div 20\text{K})$. This equation is optimal for liquid crystals (LC, $\phi \approx 9$), ODICs ($\phi = 9 - 15$), selected clearly uniaxial low molecular liquid (LMW), polymers (P) for which $\phi = 9 - 12$ and spin-glass-like systems (SGLs) where $\phi = 9 - 12$ ^{22,23,37}. For the latter it is often assumed, by convention, that $T_c = T_g$ ³.

Basing on refs. 13,23 one can write the following set of equations:

$$\frac{1}{I_{DO}(T)} = \begin{cases} \left(\frac{1}{T_0}\right)T - 1 \rightarrow (\text{VFT}) \\ \left(\frac{1}{\phi}\right)T - \frac{T_c}{\phi} \rightarrow (\text{Crit.})/\text{approx.}/ \\ \left(\frac{1}{C}\right)T \rightarrow (\text{WM,MYEGA}) \\ \frac{1}{D-1} = \text{const} \rightarrow (\text{AB}) \end{cases} \quad (6)$$

$$\frac{1}{I_{DO}(T)} = \begin{cases} \left(\frac{1}{T_1}\right)T^2 \rightarrow (\text{FF1}) \\ \frac{T}{T_2 - T} \rightarrow (\text{FF2}) \end{cases} \quad (7)$$

where *FF1* and *FF2* are “formal functions”, without the physical background, introduced by Hecksher et al.¹³ to show superiority of the description without the finite-temperature divergence (below T_g) over the VFT parameterization. The “crit.” case is for the asymptotic approximation.

The MYEGA (WM)²⁰ equation is given via $\tau(T) = \tau_0 \exp[(K/T) \exp(C/T)]$ and the AB³⁶ relation by $\tau(T) = \tau_0 \exp(A/T^D)$. Is notable that relations in eq. (7), related to formal functions (*FF1* and *FF2*) proposed by Hecksher et al.¹³, do not follow the

linear behavior, i.e. $1/I_{DO}(T) \neq aT + b$. For the VFT and “critical-like” dependences $1/I_{DO}(T)$ is the linear function for which both $a \neq 0$ and $b \neq 0$. For AB equation $1/I_{DO}(T) = 1/(D-1) = b = \text{const}$ and for MYEGA (WM) dependence $1/I_{DO}(T) = (1/C)T = aT$. The list of systems for which $\tau(T)$ experimental data are analyzed in the given report is presented in Table 1, where abbreviations, full names, and symbols used in plots are listed.

The analysis based on derivation of experimental data always leads to a notable scatter in the output. To reduce this artifact, an innovative numerical analysis based on the Savitzky-Golay numerical filtering idea, introduced in refs. 22,23, was applied.

Results and discussion

Fig. 1 presents the evolution of the reciprocal of the DO index determined from $\tau(T)$ data for 42 molecular liquids explored earlier in Hecksher et al.¹³ report. For all ultraviscous systems the linear behavior of $1/I_{DO}(T) = b + aT$ takes place. Such behavior proves that using of *FF1* and *FF2* functions for these systems, suggested as optimal one in ref. 13, is unjustified. (see the non-linear temperature dependence for eqs. 6, 7)

Fig. 2 shows that coefficients $a \neq 0$ and $b \neq 0$ for all system presented in Fig. 1. Hence, in each case the evolution of $\tau(T)$ is associated with the finite temperature divergence behaviour²³. Fig. 2 contains also results for supplementary 13 glass formers in the ultraslow domain, covering liquid crystals, plastic crystals, polymers and spin glasses²³. The linear regression fit can yield values of a and b and subsequently the unequivocal estimations of the singular temperature T_N via $I_{DO}(T = T_N)^{-1} = 0$ and the coefficient $n = -(1/b) = -1/I_{DO}^{-1}(T=0)$ ²³. They can be used as the basic input parameters for the following generalized temperature dependence of the configurational entropy²³:

$$S_C(T) = S_0 \left(1 - \frac{T_N}{T} \right)^n \quad (8)$$

The summary of calculated results is presented in the Table in Supplementary Material, where values of n , m , T_N , and T_g are given.

The discussion of eq. (8), including the link to the local symmetry and the possibility of unified presentation of experimental data ranging from plastic crystal to liquid crystals via polymers and low molecular liquid crystals is presented in ref. 23.

The graphical summary of key results for all (55) tested glass formers is presented in Fig. 3. There are three characteristic domains in Fig. 3:

- (i) $n \approx 3/2$ takes place in system with molecular uniaxiality and then local orientation ordering. They are LCs, polymers like polystyrene and selected molecular liquids. These systems obey the critical-like description with a singular temperature $T_N = T_c$
- (ii) $n \approx 0.2$ is obtained for systems with dominating positional symmetry. This is the case of ODICs and SGLs where molecules are positionally ordered in the crystalline network but can more or less freely rotate. These systems obey the critical-like description with the singular temperature $T_N = T_c$
- (iii) $n \approx 1$ is valid exclusively for the VFT equation. It seems that such parameterization is acceptable only for materials with molecular without a specific symmetry. In this case the singular temperature $T_N = T_0$.

Hence, the generalized configurational entropy eq. (8) is able to capture the dynamics of any glass former discussed in this report, with the power exponent n ranging from ca. 0.2 to 3/2.

It is notable that experimental $\tau(T)$ data used by Hecksher et al.¹³, are characterized by the average value of the coefficient $n \approx 1.2$. Hence they are inherently shifted towards the model showing elements of “uniaxial, orientational symmetry,” and the VFT param-



Table 1 | Glass-forming liquids collected from refs. 13 and 23 which are included in the present analysis. The system abbreviations, name of each liquid as well as the symbol are listed. The symbols are those used in Figs. 1–2. More detailed information is provided in the Supplementary Information

| No | Systems | Full name | Symbol |
|----|------------------------|--|--------|
| 1 | 3Ph1P | 3-phenyl-1-propanol | □ |
| 2 | 3Sty | 3-styrene | ○ |
| 3 | 5-PP | 5-polyphenyl-ether | △ |
| 4 | AFEH | 2-phenyl-5-acetomethyl-5-ethyl-1,3-dioxocyclohexane | ▽ |
| 5 | BePh | benzophenone | ◇ |
| 6 | BN | butyronitrile | ▽ |
| 7 | BP2IB | biphenyl-2-yl-isobutylate | ◇ |
| 8 | BPC | 3,3,4,4-benzophenonetetra carboxylic dianhydride | ◇ |
| 9 | Cum | isopropyl-benzene | ○ |
| 10 | dBAF | dibutyl-ammonium-formide | ☆ |
| 11 | DBP | dibutyl-phthalate | □ |
| 12 | DC704 | tetraphenyl-tetramethyl-trisiloxane | □ |
| 13 | DCHMMS | dicyclohexyl-methyl-2-methylsuccinate | ○ |
| 14 | DEP | diethyl-phthalate | △ |
| 15 | DHIQ | decahydroisoquinoline | ▽ |
| 16 | dIBP | di-iso-butyl-phthalate | △ |
| 17 | DMP | dimethyl-phthalate | ▽ |
| 18 | DOP | dioctyl-phthalate | ◇ |
| 19 | DPG | dipropylene-glycol | ◇ |
| 20 | DPGDME | dipropylene-glycol-dimethyl-ether | ◇ |
| 21 | EH | 2-ethyl-hexylamine | ☆ |
| 22 | ER | diglycidyl-ether-of-bisphenol A (epoxyresin) | □ |
| 23 | FAN | 3-fluoro-aniline | □ |
| 24 | Gly | glycerol | ○ |
| 25 | KDE | cresolphthalein-dimethylether | △ |
| 26 | mTC | m-tricresyl-phosphate | △ |
| 27 | MTHF | 2-methyl-tetrahydrofurane | △ |
| 28 | mTol | m-toluene | ▽ |
| 29 | OTP | o-terphenyl | ◇ |
| 30 | PDE | phenolphthalein-dimethylether | ◇ |
| 31 | PG | 1,2-propandiol (propylene-glycol) | ○ |
| 32 | PHIQ | perhydroisoquinoline | ☆ |
| 33 | PPG | polypropylene-glycol | ○ |
| 34 | PT | pyridine-toluene | □ |
| 35 | Sal | phenyl-salicylate (salol) | ○ |
| 36 | SB | sucrose-benzonate | △ |
| 37 | Sqa | squalane | △ |
| 38 | TCP | tricresyl-phosphate | △ |
| 39 | tNB | trisnaphthylbenzene | ▽ |
| 40 | TPE | triphenyl-ethylene | ◇ |
| 41 | TPG | tripropylene-glycol | ◇ |
| 42 | Xyl | xylitol | ◇ |
| 43 | C8-OH | cyclooctanol | ● |
| 44 | C7-OH | cycloheptanol | ● |
| 45 | Cnc6 | cyanocyclohexane | ● |
| 46 | Cnadm | cyanoadamantane | ● |
| 47 | NPANPG _{0.30} | neopentylalcohol – neopentylglycol(32%) | ● |
| 48 | SG | Ferrofluid with 5% of Fe _{1-x} C _x (x = 0,2,0,3) | ▽ |
| 49 | 8*OCB | isooctylcyanobiphenyl | ▲ |
| 50 | E7 | eutectic mixture of 4 nematic LC | ▲ |
| 51 | 5*OCB | Isopentylcyanobiphenyl | ▲ |
| 52 | Srb | sorbitol | ■ |
| 53 | PS700 | Polystyrene(M _w ≈ 700) | □ |
| 54 | Prop | 1-Propanol | ■ |
| 55 | Eth | Ethanol | ■ |

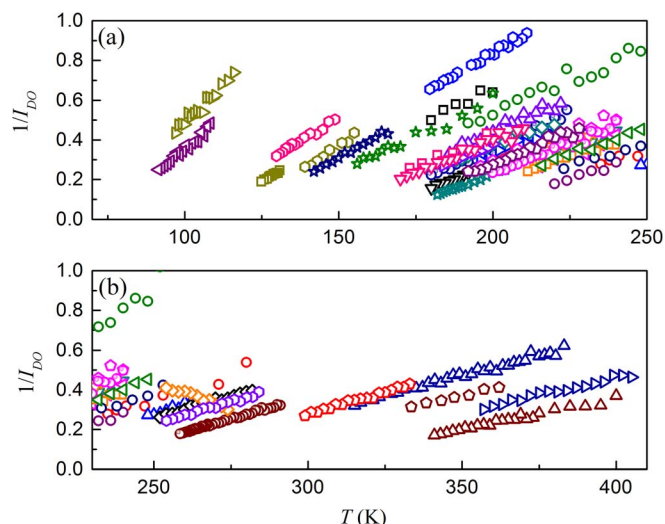


Figure 1 | Reciprocal temperature dependence of the DO index. The analysis has been done using the same sets of $\tau(T)$ experimental data by Hecksher et al.¹³. The figure is divided in two different temperature ranges (a) and (b) as was reported by Hecksher et al.¹³. Characteristics of liquids related to the given symbol are presented in Table 1.

terization is inherently non-optimal for the vast majority of molecular liquids discussed in ref. 13. It is worth recalling here that implementation of the linearized derivative based analysis^{23,33} showed that for compounds characterized by $n = 1.2 - 1.4$ both VFT and critical-like descriptions can yield comparably reliable fits of experimental data. However for $n \approx 1$ and $n \approx 3/2$ the prevalence of the VFT and critical like parameterizations, respectively, are clear (see also ref. 23).

Results of this report and ref. 23 clearly show that the VFT equation can be considered as the optimal model exclusively for systems characterized by $n = 1$. Consequently, for supercooled glass forming

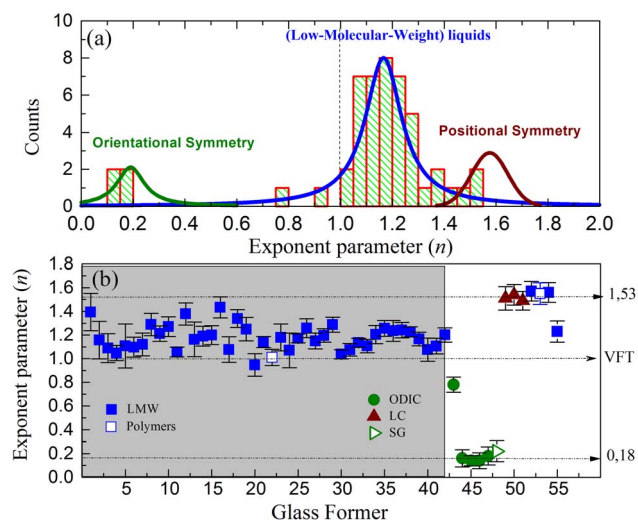


Figure 3 | Summary of the data dynamics analysis. The analysis focuses on the evolution of the parameter (n) for different groups of compounds. Fig. 3a shows the histograms of liquid systems for both groups of data. Fig. 3b illustrates the evolution of the coefficient (n) arranged according to the nomenclature in Table 1.

systems where $n \neq 1$ the implementation of the VFT equation can yield only “effective” values of D_T and T_0 , and thus the latter must differ from the Kauzmann temperature. This may be recognized as the source of fundamental discrepancy between T_0 and T_K discovered by Tanaka¹⁴, as well as noted by him linear dependence between T_0/T_K and D_T .

Fig. 4b shows that the fundamental discrepancy found by Tanaka can be absent if the “dynamic singular temperature” is determined without an underlying model-equation, i.e. as T_N from the $1/I_{DO}(T)$ plot. In such case, $T_N/T_K \approx 1$ for glass formers characterized by the

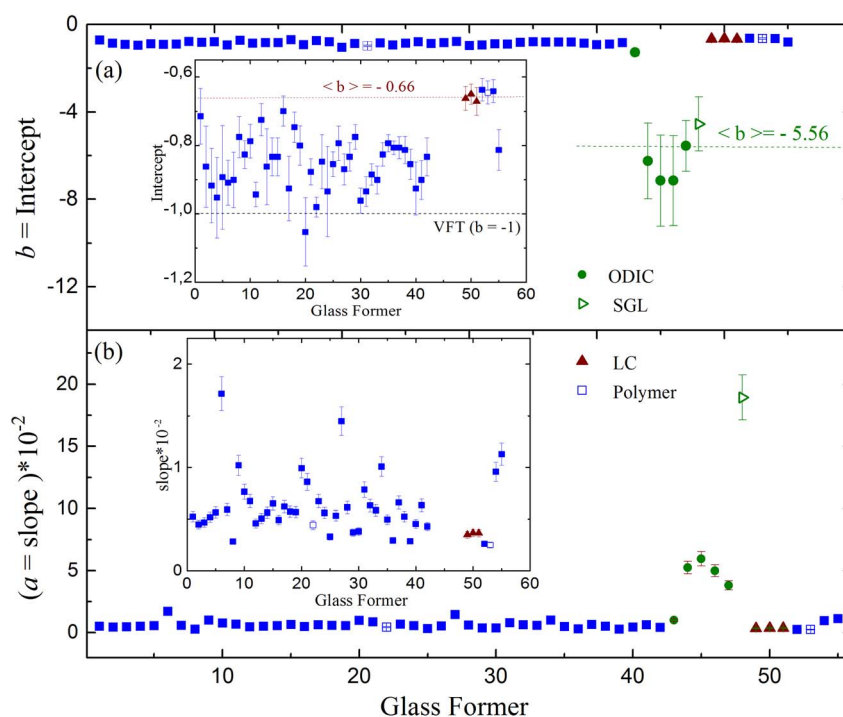


Figure 2 | Results of the linear regression analysis of $1/I_{DO}(T)$ plot for the 55 glass formers under study. Results are for the ultraviscous/ultraslowing domain. The non-zero values of coefficients a and b for $1/I_{DO}(T) = aT + b$ dependence are shown, with error bars, for all experimental sets of experimental data from ref. 13 by Hecksher et al. as well as for data from ref. 23.

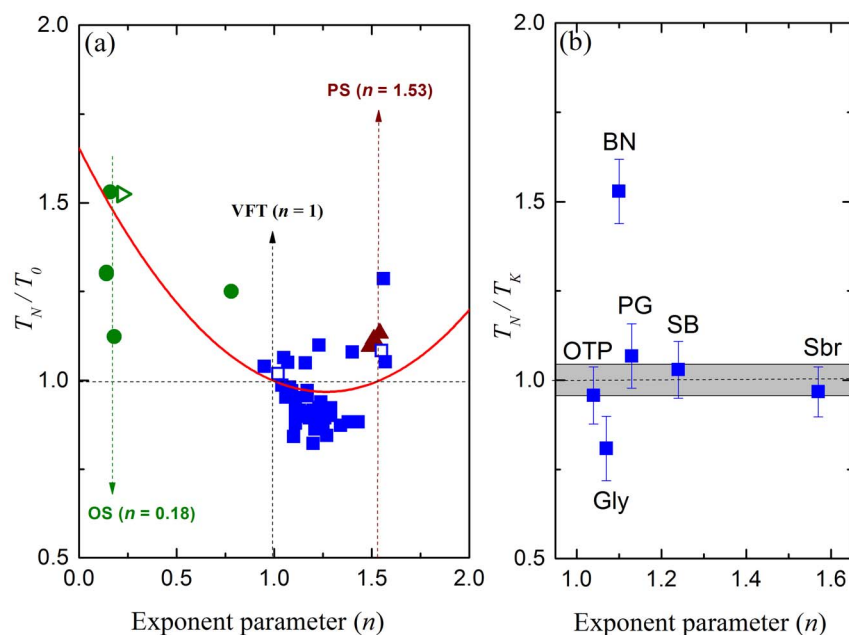


Figure 4 | Comparison among the singular T_N , T_K , and T_0 temperatures. Part (a) compares the values of T_N with T_0 , where the latter was estimated via the VFT parameterization. Part (b) shows the comparison between the singular temperature estimated via $I_{DO}(T = T_N)^{-1} = 0$ and values of the Kauzmann temperature taken from ref. 2 by Tanaka. “PS” means positional symmetry, “OS”- is for the orientational symmetry and VFT is linked to the “no-symmetry” (NS) case.

arbitrary values of n . The left part of Fig. 4 shows notable discrepancy between T_N and T_0 , particularly for “critical-like” borders ($n \approx 0.2$ and $n \approx 3/2$) and the coincidence when $n \rightarrow 1$. Hence the analysis via $1/I_{DO}(T)$ plot offers a new tool for estimating the Kauzmann temperature from “dynamic” experimental $\tau(T)$ or $\eta(T)$ data. Fig. 4 also indicates that it is possible to estimate the Kauzmann temperature even for glass forming LCs, ODICs, uniaxial polymers and SGLs: in this case $T_N = T_C = T_K$.

Conclusions

Temperature evolutions of the primary relaxation time $\tau(T)$ or viscosity $\eta(T)$ in the ultraviscous domain are the most often tested and discussed experimental artifact in the glass transition physics. The way of their portrayal is considered as one of key references for still puzzling theoretical modelling^{3–6,13–25,30–33,38–40}. Notwithstanding, amongst glass transition researchers a discouraging conviction exists that comparisons of fitting quality of $\tau(T)$ or $\eta(T)$ data with different model-equations, so far carried out mainly via the residual analysis, is likely not to be conclusive. This is strengthened by the fact that the glass transition occurs at a substantial temperature away from the putative divergence^{2,3}.

However, few years ago Dyre et al.^{13,24} proposed an innovative solution of this problem, namely the transformation of $\tau(T)$ or $\eta(T)$ experimental data to the case-sensitive apparent activation energy temperature index form $I_{DO}(T) = -d \ln \Delta E_a(T) / d \ln T$. The subsequent analysis of $\tau(T)$ data for 42 low molecular weight liquid disqualified the general validity of the VFT parameterization. The successful implementation of FF1 and FF2 formal functions, without a finite temperature divergence, became a new inspiration for the glass transition physics in last years¹³. This report and the preceding ref. 23 recall this concept, with some notable improvements:

(i) the new way of determining the apparent activation energy $\Delta E_a(T)$ and then $I_{DO}(T)$, avoiding the biasing impact of τ_0 in the SA eq. (1), was introduced (see Supplementary information). It was supported by numerical filtering based on Savitzky-Golay principle²³. This routine can yield non-biased values of $\Delta E_a(T)$ and $I_{DO}(T)$ from $\tau(T)$ or $\eta(T)$ experimental data.

- (ii) The analysis was focused on the reciprocal of the apparent activation energy temperature index, since it appeared that for all 55 glass formers: $1/I_{DO}(T) = a + bT$ with $a \neq 0$ and $b \neq 0$.
- (iii) The analysis covered not only a single category of glass formers but also liquid crystals, plastic crystals (ODIC) or even spin-glass-like systems.

Regarding relations without a “finite temperature divergence”: BA^{34,35} or WM (MYEGA)^{20,36} equations are related to coefficients $b = 0$, $a = 0$ and FF1 and FF2 functions¹³ $1/I_{DO}(T)$ follows a nonlinear dependence (see eqs. 6, 7). Such behavior is in clear disagreement with the experimental evidence presented above. The fact that experimental $1/I_{DO}(T)$ dependences follow solely a linear dependence, allow for the unequivocal determining of the “dynamics divergence temperature” via $1/I_{DO}(T = T_N) = 0$, i.e. $T_N = a/b$ condition.

The extension of analysis for few categories of glass forms (this report and ref. 23) led to finding a new general metric $0.18 < n = -1/I_{DO}^{-1}(T = 0) < 1.6$. Value $n \approx 0.18$ is related to ultraslowing systems with dominated positional symmetry (ODICs.) and $n \approx 1.6$ for systems with dominated orientational symmetry (LCs, ...). For these ultraslowing systems the critical-parameterization yields a reliable approximation (see also ref. 23).

The VFT equation is optimal only for a limited number of glass formers where $n = 1$. These facts show that direct “fitting goodness” comparisons between VFT and other model equation based on $\tau(T)$ or $\eta(T)$ experimental data for arbitrary selected glass formers are inherently non-conclusive. Values of the coefficient n , the singular temperature T_N as well as T_g and fragility m for 55 tested glass formers are given in the Table in Supplementary Information.

It is notable that the VFT relation appears to be the optimal for the limited number of glass forming systems where $n = 1$. For glass former characterized by $n \neq 1$, the VFT equation can serve solely as an empirical, effective, tool for parameterization. Consequently, we postulate that results assuming the general validity of the VFT equation should be reanalyzed, particularly regarding discussions involving T_0 or D_T parameters refs. 3–6,38–40 as well as refs. recalled therein.



Results of this paper also yield the possibility of solving one of the most important cognitive problems of the glass transition physics, namely the discrepancy between the “dynamic”, i.e., based on the VFT equation, and “thermodynamic” (from heat capacity data) estimations of the ideal glass (Kauzmann) temperature. These estimations match if the “dynamic” estimation is based on the model-independent way of analysis, via the $1/I_{DO}(T)$ plot. All these can be essential for the theoretical modeling^{2–6} and may also lead to questions regarding features of the amorphous glass state in domains $T_N = T_K < T < T_g$ and $T < T_N$. The fundamental plot in ref. 14 by Tanaka showing the linear dependence of T_K/T_0 vs. D_T , with $0.5 < T_K < T_0 < 2.2$, resulted from the mentioned inadequacy of the VFT equation. It is notable that results presented by Tanaka omitted LCs, ODICs or SGLs, where VFT equation cannot yield even the effective reliable parameterization.

Results of this report, supplemented by ref. 23, show that the still dominated in the glass transition and soft matter physics, VFT equation or its parallels like Williams-Landolt-Ferry (WLF) equation, can be considered only as an “effective tool” for portraying experimental data. Their parameters has a clear physical meaning only for the limited number of system characterized by $n = 1$. Otherwise, values of D_T and T_0 are biased and have the meaning of an “effective fitting parameter”. All these can indicate that numerous research reports based on the general validity of the VFT equation should be reconsidered.

In 1995 Philip W. Anderson, a Nobel Prize-winning physicist, wrote⁴¹: “The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition. This could be the next breakthrough in the coming decade.” But the long awaited breakthrough is still postponed...^{1,3,4,6,7}. One of clearly formulated reasons is the extremely sophisticated and complex new physics behind the glass transition^{2–7}. But the delay of the long awaited breakthrough may be also associated with the model-dependent insight which may bias or even hide fundamental artifacts. In this report we propose the new, model-free route.

- Kennedy, D. 125 outstanding problems in all of science: what is the nature of the glassy state. *Science* **309**, 83 (2005).
- Mauro, J. Viscosity of glasses and glass forming liquids. in Diverging and non-diverging time-scales session, p. 1, *Abstracts of 7th International Discussion Meeting on Relaxations in Complex Systems*. 21–26 July 2013, Barcelona, Spain (UPC, Barcelona, 2013).
- Ngai, K. L. *Relaxation and Diffusion in Complex Systems* (Springer, Berlin, 2011).
- Stillinger, F. H. & Debenedetti, P. G. Glass transitions: thermodynamics and kinetics. *Annu. Rev. Cond. Matt. Phys.* **4**, 262–270 (2013).
- Jones, R. A. L. *Soft Condensed Matter* (Oxford Univ. Press, NY, 2002).
- Berthier, L. & Biroli, G. Glasses and aging: a statistical mechanics perspective. in: *Encyclopedia of Complexity and Systems Science* (ed. by Meyers, R. A.), 4209–4240 (Springer, 2009).
- Mauro, J. Glass: The nanotechnology connection. *Int. J. Appl. Glass Sci.* **4**, 64–75 (2013).
- Chaudhuri, U. R. *Fundamentals of Petroleum and Petrochemical Engineering* (CRC Press, 2011, Boca Raton (FL, USA)).
- Thomas, S. A. & Zachariah, K. *Polymer Processing and Characterization* (Apple Academic Press, Boca Raton (FL, USA) 2012).
- Jadhav, N. R., Gaikwad, V. L., Nair, K. J. & Kadam, H. M. Glass transition temperature: Basics and application in pharmaceutical sector. *Asian J. Pharm.* **3**, 82–89 (2009).
- Roos, Y. H. Glass transition temperature and its relevance in food processing. *Ann. Rev. Food Sci. & Technol.* **1**, 469–496 (2010).
- Poirier, J.-P. *The Introduction to Physics of Earth Interior* (Cambridge Univ. Press, Cambridge UK, 2000).
- Hecksher, T., Nielsen, A. I., Olsen, N. B. & Dyre, J. C. Little evidence for dynamic divergences in ultraviscous molecular liquids. *Nature Phys.* **4**, 737–741 (2008).
- Tanaka, H. Relation between thermodynamics and kinetics of glass-forming liquids. *Phys. Rev. Lett.* **90**, 05570 (2003).
- Kauzmann, W. The nature of the glassy state and the behavior of liquids at low temperatures. *Chem. Rev.* **43**, 219–256 (1948).
- Andersen, H. C. Molecular dynamics studies of heterogeneous dynamics and dynamic crossover in supercooled atomic liquids. *Proc. Natl. Acad. Sci. USA* **102**, 6686–6691 (2005).

- Eckmann, J. P. & Procaccia, I. Ergodicity and slowing down in glass-forming systems with soft potentials: no finite-temperature singularities. *Phys. Rev. E* **78**, 011503 (2008).
- Kivelson, S. A. & Tarjus, G. In search of a theory of supercooled liquids. *Nature Mater.* **7**, 831–833 (2008).
- Hedges, L. O., Jack, R. L., Garrahan, J. & Chandler, D. A. Dynamic order-disorder in atomistic models of structural glass formers. *Science* **6**, 1309–1313 (2009).
- Mauro, J. C., Yue, Y., Ellison, A. J., Gupta, P. K. & Allan, D. C. Viscosity of glass-forming liquids. *Proc. Natl. Acad. Sci. USA* **106**, 19780 (2009).
- Tanaka, H. Bond orientational order in liquids: Towards a unified description of water-like anomalies, liquid-liquid transition, glass transition, and crystallization. *Eur. Phys. J. E* **35**, 1–84 (2012).
- Martinez-Garcia, J. C., Martinez-Garcia, J., Rzoska, S. J. & Hulliger, J. The new insight into dynamic crossover in glass forming liquids from the apparent enthalpy analysis. *J. Chem. Phys.* **137**, 064501 (2012).
- Martinez-Garcia, J. C., Rzoska, S. J., Drozd-Rzoska, A. & Martinez-Garcia, J. A universal description of ultraslow glass dynamics. *Nat. Commun.* **4**, 1823 (2013).
- Dyre, J. C. & Olsen, N. B. Landscape equivalent of the shoving model. *Phys. Rev. E* **69**, 042501 (2004).
- Mauro, J. C. & Ellison, A. J. Breakdown of the fractional Stokes-Einstein relation in silicate liquids. *J. Non-Cryst. Solids* **357**, 3924–3927 (2011).
- Vogel, H. Temperaturabhängigkeitsgesetz der viskosität von flüssigkeiten. *Phys. Zeit.* **22**, 645–646 (1921).
- Fulcher, G. S. Analysis of recent measurements of the viscosity of glasses. *J. Am. Ceram. Soc.* **8**, 339–355 (1925).
- Tammann, G. Glasses as supercooled liquids. *J. Soc. Glass Technol.* **9**, 166–185 (1925).
- Angell, C. A. Strong and fragile liquids. in: *Relaxations in Complex Systems*, eds. Ngai, K. L. & Wright, G. B. (National Technical Information Service, U.S. Department of Commerce, Springfield, 1985).
- Boehmer, R., Ngai, K. L., Angell, C. A. & Plazek, J. D. Nonexponential relaxations in strong and fragile glass formers. *J. Chem. Phys.* **99**, 4201–4209 (1993).
- Adam, G. & Gibbs, J. H. On the temperature dependence of cooperative relaxation properties in glass-forming liquids. *J. Chem. Phys.* **43**, 139–146 (1965).
- Angell, C. A. Entropy and fragility in supercooling liquids. *J. Res. Natl. Inst. Stand. Technol.* **102**, 171–185 (1997).
- Drozd-Rzoska, A. & Rzoska, S. J. On the derivative-based analysis for temperature and pressure evolution of dielectric relaxation times in vitrifying liquids. *Phys. Rev. E* **73**, 041502 (2006).
- Baessler, H. Viscous flow in supercooled liquids analyzed in terms of transport theory for random media with energetic disorder. *Phys. Rev. Lett.* **58**, 767–770 (1987).
- Avramov, I. Viscosity in disordered media. *J. Non-Cryst. Solids* **351**, 3163–3173 (2005).
- Waterton, S. C. The viscosity-temperature relationship and some inferences on the nature of molten and of plastic glass. *J. Soc. Glass Technol.* **16**, 244–247 (1932).
- Drozd-Rzoska, A., Rzoska, S. J. & Paluch, M. Universal, critical-like scaling of dynamic properties in symmetry-selected glass formers. *J. Chem. Phys.* **129**, 184509 (2009).
- Stickel, F., Fischer, E. W. & Richert, R. Dynamics of glass-forming liquids. I. Temperature-derivative analysis of dielectric relaxation data. *J. Chem. Phys.* **102**, 6251–6262 (1995).
- Roland, C. M. Relaxation phenomena in vitrifying polymers and molecular liquids, conditions. *Macromolecules* **43**, 7875–7890 (2010).
- Chen, Z., Angell, C. A. & Richert, R. On the dynamics of liquids in their viscous regime approaching the glass transition. *Eur. Phys. J. E* **35**, 65 (2012).
- Anderson, P. W. Through the glass lightly. *Science* **267**, 1615–1616 (1995).

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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, J.M.G. focused in Savitzky-Golay principle based analysis of data and also in the understanding and interpretation of the developed method. 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 final were notable influenced by A.D.R. and J.C.M.

Additional information

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