# Universal relation between viscous flow and fast dynamics in glass-forming materials

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The connection between viscous flow and vibrational properties in glass-forming materials is scrutinized examining the fragility of a wide set of liquids and the nonergodicity factor of the corresponding glasses. Building on the same line of reasoning which allows us to extend the connection between viscosity and thermodynamics in complex systems, we show here how the two quantities are strongly correlated once the effect of those secondary relaxation processes due to internal degrees of freedom is correctly accounted for. This result provides a missing thermodynamic rationale for the recently debated universality of the correlation between fast and slow degrees of freedom.

Glass-forming liquids can cross the melting line avoiding crystallization, and upon cooling below the melting temperature, their viscosity increases by several orders of magnitude, eventually leading to the glass transition. This is a kinetic transition usually defined by the condition in which the structural relaxation time (the $\alpha$ process) equals a given value, arbitrarily fixed to 100 s. At the glass transition temperature, $T_g$, the shear viscosity of most systems is in the range of $10^{11} < \eta < 10^{13}$ poise, values high enough to consider the system as "solid" from the mechanical point of view.

The rapidity of the increase in the viscosity when approaching $T_g$ from the liquid side led in the scientific community to the classification of glasses into long and short,[1] a concept widespread by Angell introducing the kinetic "fragility"[2]

$$m = \lim_{T \to T_g} \frac{d \log(\eta)}{d(T_g/T)}. \qquad (1)$$

Since $\eta \approx 10^{-4}$ poise is the "infinite" temperature limit in basically any material and $\eta(T)$ is always found to be a concave function of $T^{-1}$, the lowest fragility value is around $m = 17$, and the systems in the low $m$ side are named "strong" liquids and show an Arrhenius behavior. Conversely, it is empirically found that for the most "fragile" systems, where a high (and $T$-dependent) apparent activation energy is found, $m > 150$.

Despite decisive theoretical steps forward in the comprehension of the glass transition,[3] the *phenomenological* relations associating the fragility to other physical properties still play a central role in this field, allowing to shed light on possible deep links among apparently uncorrelated quantities. Among them, (i) the thermodynamic approach to the fragility[4,5] also in the light of the Adam-Gibbs (AG) theory[6–8] and the random first-order transition;[9] (ii) the ratio between the maximum and the minimum of the boson peak, i.e., of the bump observed at the Thz frequencies in the Raman- and neutron-scattering spectra of glass-forming materials;[10] (iii) the degree of stretching in the nonexponential decay of the correlation functions in the liquid close to $T_g$ (Ref. 11); (iv) the statistics of the minima in a potential energy landscape-based description of the diffusion process in

supercooled liquids;[12,13] (v) the temperature behavior of the high frequency shear elastic modulus in the supercooled liquid;[14] (vi) the Poisson ratio;[15–18] (vii) the mean squared displacement in a glass, which for different systems seems to stand in the same order as they stand in a $T_g$ scaled Arrhenius plot.[19,20] In all these studies, the fragility has been always related to macroscopic properties on approaching the glass transition from the *liquid* side.

Interestingly, a similar correlation has also been found with *low-temperature* vibrational properties, specifically with the nonergodicity factor (NEF) $f(Q,T)$ the plateau (i.e., the long time limit) of the autocorrelation function of the density fluctuations, $\phi(Q,t)$. In Ref. 21, indeed, it was shown that (i) the NEF can be obtained in the frequency domain by means of inelastic x-ray scattering (IXS) by measuring the ratio between inelastic ($S_{inel}(Q)$) and elastic ($S_{IS}(Q)$) scattering contributions and that (ii) the low-temperature dependence of the NEF follows the law, deduced by an harmonic description of the atomic vibrations:

$$f(Q,T) = \lim_{t \to \infty} \phi(Q,t) = \frac{1}{1 + \dfrac{S_{inel}(Q)}{S_{IS}(Q)}} = \frac{1}{1 + \alpha \dfrac{T}{T_g}}, \qquad (2)$$

and, most important, (iii) a direct proportionality

$$m \propto \alpha \qquad (3)$$

(with a proportionality factor $\approx 135$) holds, meaning that the NEF of a glass *well below $T_g$*, (in the $T \to 0$ limit) is correlated with the fragility value, i.e., a property of the liquid determined approaching $T_g$ *from above*. This observation provides a way to extend the fragility concept to the glassy state and, in principle, indicates how to determine the fragility uniquely from glass properties well below $T_g$. It was soon realized, however, that the NEF determined in a similar way in some complex systems does not obey the proposed linear correlation,[18,22,23] a result recently discussed in the light of isobaric vs isochoric definition of fragility.[24]

In this work, we demonstrate how this apparent failure is hidden in the break down of the validity of Eq. (2) in polymers and complex systems. Most important, we show how to get rid of these additional contributions, eventually restoring
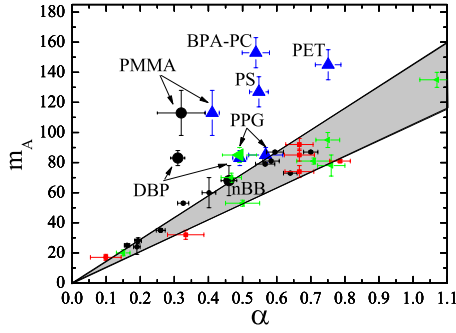
FIG. 1. (Color online) Correlation between the temperature dependencies of relaxation time (fragility, $m$) and NEF ($\alpha$). This latter was determined assuming that a single (structural) relaxation governs the microscopic dynamics using: IXS [black circles, in order of increasing fragility: NiZr, BeF$_2$, Silica, Cyanadamantane, glycerol, 1,4 polybutadiene (1,4PB), normal-butylbenzene, salol, $m$-toluidine, $o$-terphenyl (OTP), selenium and $m$-tricresylphosphate (mTCP)] (Ref. 21). Compressibility measurements from Brillouin spectroscopy [blue up triangles, in order of increasing fragility: dibutypthalate, poly(propylene glycol) (PPG), PMMA, PS, PET, BPA-PC] (Ref. 22), Photon correlation spectroscopy (red squares, in order of fragility: As$_2$O$_3$, B$_2$O$_3$, 0.5Li0.5NaPO$_3$, OTP, NaPO$_3$, and LiPO$_3$) (Ref. 25). Sound velocity jump at $T_g$ [green left triangles, in order of increasing fragility: germanium dioxide (GeO$_2$) (Refs. 11 and 26); propylene glycol (PG) (Refs. 11 and 36); poly(butyl acrylate) (PBA) (Refs. 27 and 28); poly(propylene glycol)-diglycidylether (PPGDE) (Refs. 29 and 30); poly(propylene glycol) (PPG) (Refs. 31 and 32); diglycidyl ether of bisphenol A (DGEBA) (Refs. 33 and 34); 1,2 polybutadiene (1,2PB) (Refs. 11 and 35)]. Large symbols, explicitly labeled, are used for those system having nonzero residual entropy at the Vogel temperature, i.e., subject to a correction according to Eq. (5). Shaded area represents values $105 < \alpha < 145$.

the universal validity of prediction (3). In Fig. 1, we report the $\alpha$ factor for several systems determined by means of different techniques: (i) measuring the inelastic/total scattering ratio by means of IXS through Eq. (2) (black symbols), (ii) directly measuring the plateau of the density autocorrelation function (DAF) in the time domain via photon correlation spectroscopy (red symbols, from Ref. 25), (iii) evalu-

ating the sound velocity jump at the glass transition temperature $c_{liquid}(T \to T_g^+)/c_{glass}(T \to T_g^-)=c_0(T_g)/c_\infty(T_g)$ by means of Brillouin light scattering and ultrasonics (green symbols) or compressibility ($\chi$) measurements (blue symbols) via the expression:[22]

$$f(Q,T) = 1 - \left.\frac{c_0^2}{c_\infty^2}\right|_{T_g} = 1 - \left.\frac{1}{\rho\chi c_\infty^2}\right|_{T_g}. \qquad (4)$$

Within the above framework, one implicitly assumes that the quantities measured in the time/energy windows of the experiment are solely related to the structural relaxation (hence to the ergodicity breaking), which is certainly true if this is the only (or at least the dominant) process governing the dynamics upon approaching the glass transition. Focusing on the determination of $f(Q)$ through the elastic/total ratio in dynamic structure fator (DSF) measured by IXS, for instance, the presence of additional slow[37] processes arising from some internal degrees of freedom pile up the quasielastic contribution of $S_{inel}(Q)$ leading to an incorrect determination of the NEF. This is elucidated in Fig. 2, where we show how the decay of the DAF in the time domain can occur in multiple steps in presence of secondary relaxations (hereafter labeled as $\beta$) and, consequently, the Fourier transform-related ratio $S_{inel}/S_{IS}$ cannot be directly utilized to extract the NEF which is the last plateau of the decay being related to the structural relaxation only. Hence, one can easily introduce the decomposition $S_{IS}=S_{IS,\alpha}(Q)+S_{IS,\beta}(Q)$ and, from Eq. (2), the correct candidate to be correlated with fragility will be $\tilde{\alpha}=\frac{T_g}{T}\frac{S_{inel}(Q)}{S_{IS,\alpha}(Q)}$, which can be expressed in terms of the *total* (measured) $\alpha$ as

$$\tilde{\alpha} = \frac{S_{IS}(Q)}{S_{IS,\alpha}(Q)}\alpha. \qquad (5)$$

The scenario sketched in Fig. 2 can be considered highly realistic. It is in fact well known that, for some glass-forming polymers possessing secondary relaxation processes as detected by dynamic-mechanical spectroscopy,[38] such secondary relaxations can account for as much as 70% of the total relaxation [see, e.g., polymethyl methacrylate (PMMA) in
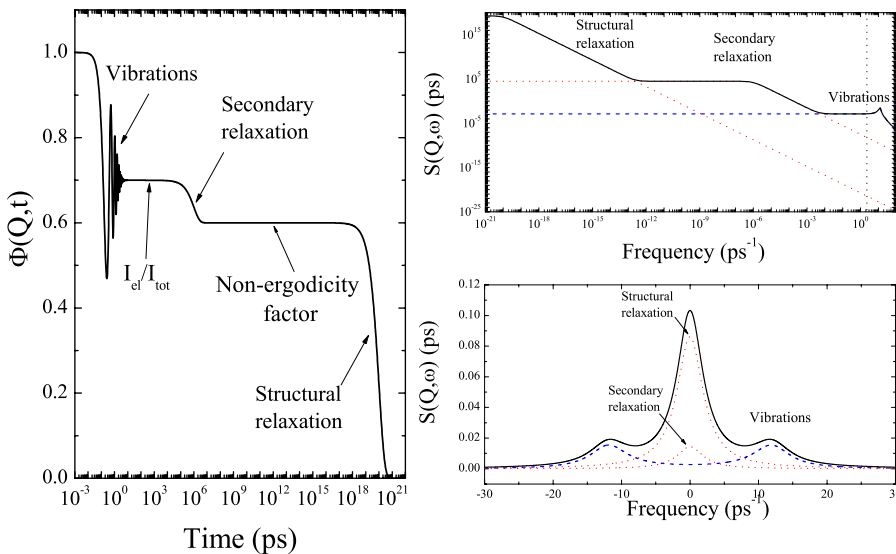


FIG. 2. (Color online) Toy model illustrating how the presence of a secondary relaxation affects the DAF. Left panel: DAF in presence of an additional "slow" relaxation. Right upper panel: the corresponding DSF (black line). Vibrational contribution (dashed blue line) and structural and secondary relaxations (dotted red lines) are also indicated. The vertical dotted black line indicates the inverse of the typical resolution linewidth. In the right bottom panel we report (with the same notations) the DSF convoluted with the instrumental resolution, i.e., as measured in an IXS experiment.

Fig. 8.12 of Ref. [38]). In all those polymers not fulfilling the fragility vs the $\alpha$ factor relation, it is important to notice that secondary relaxations account for at least 20% of the total relaxation.[38] In the case of polymers and other complex glass formers possessing prominent secondary relaxations, the NEF (the plateau of the autocorrelation function in the glassy limit) does not coincide with the long time limit of the vibrational contribution. In the frequency domain, this implies the presence of two different contributions to the quasielastic line which cannot be resolved when the time scale of the additional relaxations is much longer than the inverse instrumental resolution linewidth. In such cases, these processes cannot be disentangled through an IXS experiment, and measured elastic/inelastic ratio provides an overestimate of the true, structural relaxation related, NEF, leading to an underestimate of the $\alpha$ parameter.[39]

This observation can explain, for instance, the scattering of the points of $m$-$\alpha$ in Fig. [1] for several glass-forming polymers, which has been pointed out in Ref. [22]. Apart from polymers, a similar scenario emerges in the case of low molecular weight glass formers such as dibutylphtalate (DBP), $n$-buthylbenzene ($n$-BB) and decahydroisoquinoline (DHIQ), showing a deviation from Eq. (3) (Refs. [40] and [41]) which can be explained by the presence of two secondary relaxation processes.[42]

The question that we pose now is how can one identify those systems with secondary relaxations and is there a way to estimate the correction factor appearing in Eq. (5). The unsettling effect of secondary relaxations on the empirical correlations involving fragility is not new: the correlation between fragility and the specific heat jump at $T_g$ was also found to break down in polymers.[43,44] The concept of thermodynamic fragility, $m_T$, indeed, was introduced observing that the behavior displayed by the excess entropy ($\Sigma_{ex}$, defined as the difference between the entropy of the liquid and the entropy of the underlying crystalline structure) in a $T_g/T$ scaled plot, closely resembles that of viscosity (or structural relaxation time).[4] In view of such similarity, the thermodynamic fragility index was defined as

$$m_T = \lim_{T \to T_g} \frac{d[\Sigma_{ex}(T_g)/\Sigma_{ex}(T)]}{d(T_g/T)} = T_g \frac{\Sigma'_{ex}(T)}{\Sigma_{ex}(T_g)} = \frac{\Delta c_p(T_g)}{\Sigma_{ex}(T_g)}. \quad (6)$$

A way to explain the observed correlation between $m$ and $m_T$ it is naturally provided by the Adam-Gibbs relation, connecting the structural relaxation time and the configurational entropy, $\Sigma_c$ as: $\tau = \tau_0 \exp(\frac{A}{T\Sigma_c})$. Within the widely accepted assumption of direct proportionality between excess entropy and configurational entropy,[45–47] plugging AG into Eq. (1) and defining $R_\infty = \log(\tau(T_g)/\tau_\infty)$ one immediately gets

$$m = R_\infty(m_T + 1). \quad (7)$$

Interestingly, Eq. (7) fails in several complex glass formers. It has recently been proposed by Cangialosi *et al.*[8,48] that the reason for such failure can be traced back to the presence of a residual excess entropy at the Vogel temperature $T_0$, namely, to the difference between the Kauzmann temperature $T_K$ and $T_0$. As, according to the AG relation, at $T_0$ no $\alpha$ relaxation-related excess entropy should be left out, the re-
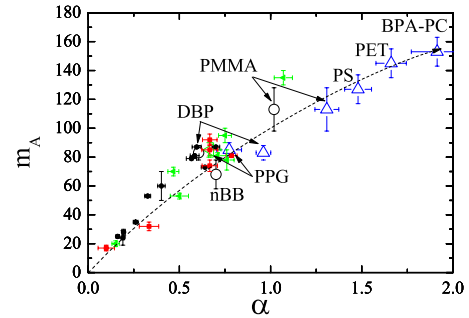


FIG. 3. (Color online) Correlation between the temperature dependencies of relaxation time (fragility, $m$) and NEF ($\alpha$) accounting for the presence of secondary relaxations. The $\alpha$ parameter was indeed corrected through Eqs. (5) and (10) for all polymers possessing secondary relaxation processes plus DPB and $n$-BB. Notations are the same as in Fig. [1].

sidual excess entropy at $T_0$ has been attributed to non-$\alpha$ process related relaxational processes arising from internal degrees of freedom.[8,48] In particular, it has been shown that relation (7) is restored by considering the residual excess entropy related to the structural relaxation only:[8,48]

$$m = R_\infty \left[ T_g \frac{\Sigma'_{ex}(T_g)}{\Sigma_{ex}(T_g) - \Sigma_{ex}(T_0)} + 1 \right] = R_\infty \left[ T_g \frac{\Sigma'_{ex}(T_g)}{\Sigma_{ex,\alpha}(T_g)} + 1 \right]$$

$$= R_\infty[\tilde{m}_T + 1], \quad (8)$$

in which

$$\tilde{m}_T = \frac{\Sigma_{ex}(T_g)}{\Sigma_{ex,\alpha}(T_g)} m_T \quad (9)$$

is the contribution to the thermodynamic fragility due to the structural relaxation. The similarity of Eqs. (5) and (9) suggests that the factor $\frac{S_{IS}(Q)}{S_{IS,\alpha}(Q)}$, which is a measure of the extra "amount of decorrelation" induced by secondary relaxations, may have a thermodynamic origin. This decorrelation, indeed, has to be related to the different decay channels, i.e., to the number of energy minima, associated to the secondary relaxations once the structural process is frozen out. The most obvious way to quantify this effect, is counting the logarithm of this number, i.e., via the contribution of the secondary relaxation to the excess entropy:

$$\frac{S_{IS}(Q)}{S_{IS,\alpha}(Q)} = \frac{\Sigma_{ex}(T_g)}{\Sigma_{ex,\alpha}(T_g)} = \frac{\Sigma_{ex}(T_g)}{\Sigma_{ex}(T_g) - \Sigma_{ex}(T_0)}. \quad (10)$$

In Fig. [3] we show a $m$-$\alpha$ plot in which the alpha values have been corrected according to Eq. (5) (*only* for those systems having residual excess entropy to account for the net effect of the structural relaxation). The values of the excess entropy at $T_g$ and $T_0$ are taken from Refs. [8] and [48–50]. A linear correlation is clearly restored, also accounting for the experimental indetermination which often affects even the same system measured by different techniques. Moreover, the correlation is compatible with that proposed for low molecular weight glass formers. Although the correction leading from $\alpha$ to $\tilde{\alpha}$ probably overestimates the effect of secondary relaxation it certainly goes in the right direction.

In conclusion, we addressed in this Rapid Communication the relation between slow dynamics (viscous flow) and non-ergodicity factor of the glassy phase. This is an unanswered question of paramount importance in glass-forming materials science because of its consequences on the topology of the potential energy landscape (distribution and shape of energy minima). Specifically, we demonstrated the correlation between the fragility of a liquid and the vibrational properties of the corresponding harmonic amorphous solid to be a universal feature of the glass formation process. This is consistent with the idea that the viscous slowing down accompanying the glass transition is intimately related to the topology of those minima explored during the structural arrest, while there is no correlation with the properties of minima visited due to secondary relaxation mechanisms. The fraction of this latter minima, which quantifies the magnitude of the secondary processes, can be successfully accounted for by entropic arguments. This result has deep implications for the understanding of glass formation: it establishes a firm link between slow (viscosity) and fast (nonergodicity factor[21]) degrees of freedom assisted by thermodynamics, rendering the vibrational and the thermodynamic approaches to fragility essentially equivalent.

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