16

Interplay between Fragility and Glass Dynamics

Tullio Scopigno and Daniele Cangialosi

The search for a connection between the fragility, that is, the steepness of the temperature variation of the structural relaxation time [2], and other properties of glass forming liquids is currently a matter of open debate. Within this context a number of approaches have been developed in the past. Among them those based on the connection of the fragility with the thermodynamics and the low temperature vibrational properties of glass formers have been the object of our previous studies. We review here the development of these two approaches and how they have been later connected to each other.

Scopigno et al. [21] collected data on the fragility and the nonergodicity factor (NEF) for a considerable number of non-polymeric glass former. The latter was determined by measuring the elastic to inelastic scattering ratio in a IXS (Inelastic X-ray Scattering) experiment. They showed how glass formers exhibiting relatively large decorrelation at low temperatures are those very fragile. Hence a linear correlation between the fragility and a parameter (α) related to the NEF was found. Such correlation was later addressed by Buchenau and Wischnewski [3]. He showed that several glass-forming polymers do not follow the linear relation. In particular, according to Buchenau and Wischnewski's analysis, those glass-forming polymers deviating from the expected behaviour exhibit large fragilities and comparatively small α parameters.

A similar historical development can be encountered within the context of the thermodynamic approach to the fragility. Inspired by the Adam-Gibbs (AG) theory of the glass transition [1], relating the structural relaxation time (τ) with the excess entropy (Σ_{ex}): $\tau = \tau_0 exp(C/(\Sigma_{ex}T)$, Martinez and Angell [13] argued that the kinetic fragility can be correlated to the rapidity of variation of Σ_{ex}. This is one of the several ways of defining the thermodynamic fragility. Other methods rather define the thermodynamic fragility as equal to the jump of the specific heat at the glass transition temperature (T_g) [18] or the ratio of the melt and glassy specific heat [11]. Once these definitions are employed, the correlation between dynamic and thermodynamic fragilities in polymeric glass formers seems to be not fulfilled.

In view of the previous results, it was clear that both the approach based on the NEF and those relying on the connection with thermodynamics needed to be appropriately tackled for polymeric glass formers. Along this line, in an effort to extend the thermodynamic approach to determine fragility in polymeric systems, Cangialosi et al. [4, 5] re-analysed thermodynamic and dynamic data on several glass forming polymers. First of all they employed a definition of the thermodynamic fragility directly derived from the AG equation relating the structural relaxation time to the configurational entropy [19, 14, 7]:

$$m_T = \left.\frac{d[ln(\tau(T)/\tau_0)/ln\tau(T_g)/\tau_0)}{d(T_g/T)}\right|_{T_g} = 1 + \frac{\Delta C_p(T_g)}{\Sigma_{ex}(T_g)} \tag{16.1}$$

where m_T is the thermodynamic fragility. In doing so, Cangialosi et al. [4, 5] exploited the proportionality of the excess and configurational entropy [**?**], being the former directly accessible to experiments. Furthermore they neglected temperature dependence of the energy barrier per structural unit [8]. This is in fact only weakly temperature dependent in a wide range [17]. More importantly, in the analysis performed by Cangialosi et al. [4, 5], the contribution of secondary relaxation processes to Σ_{ex} was considered for those polymers where these processes are present. Such contribution was determined considering the residual Σ_{ex} at the Vogel temperature, that is, the temperature where divergence of τ is predicted [23, 9, 22]. At this temperature no contributions from the main structural relaxation processes is expected, in line with the conjectures of the AG theory stating that no configurational entropy should exist at the temperature where the relaxation time diverges. Once the contribution to Σ_{ex} from secondary relaxations is obtained in this way, the relation between the thermodynamic and dynamic fragility is restored.

Inspired by the mentioned correction to the thermodynamic fragility, Scopigno et al. [20] pointed out that estimates of the NEF based on scattering ratio in IXS experiments account solely for the decorrelation of density fluctuation due to vibrational degrees of freedom. Since the NEF is the long time plateau of the density autocorrelation function, the IXS method can only be applied in its original implementation when the only relaxation process is the structural one. In presence of secondary relaxations, faster than the structural process, intermediate additional plateau will appear in the density autocorrelation, and a meaningful connection with the fragility of the glass former should rather isolate the contribution from the structural relaxation only. In the work of Scopigno et al. [20] the degree of decorrelation resulting from secondary relaxations in the form of additional contribution in the elastic spectral response, is straightforwardly quantified based on the contribution of secondary relaxations to Σ_{ex}. In doing so, the correlation between α, a parameter directly related to the NEF, and the fragility, m, is recovered for those glass forming polymers exhibiting significant secondary relaxation processes. This result establishes a link between slow dynamics and low temperature vibrational properties [6], at ease with early observations on the mean square displacement more recently emphasized by Larini et al. [12].

All together, these findings demonstrated two important points in the description of the fragility of glass-forming liquids: i) the essential equivalence between the thermodynamic approach and that based on fast vibrational degrees of freedom; and ii) the peculiarity of polymeric glass formers due to the prominent contribution of secondary relaxations to both thermodynamic properties Σ_{ex} and the density autocorrelation function.

Several studies have been recently reporting apparent outliers of either the thermodynamic or the vibrational approach to determine the fragility, even in non-polymeric glass formers. Niss et al. [15] presented a detailed experimental study on the short wave-length properties probed by inelastic x-rays scattering (IXS) on a significant number of glass formers. They showed that decahydroisoquinoline (DHIQ), a glass former with exceptionally high fragility ($m = 155$), exhibits strong deviations from the expected relation with the α parameter obtained from the NEF. However, DHIQ exhibits a strong secondary relaxation process, as shown by dielectric relaxation spectroscopy (DRS) [16], likely related to the considerable number of intra-molecular degrees of freedom possessed by DHIQ. Hence, before drawing any final conclusions, the contribution of secondary relaxations to α should be properly accounted for. Ruta et al. presented IXS results on glassy sorbitol [**?**]. The obtained α parameter of the NEF was shown to be too small to be related to the fragility in the way proposed by Scopigno et al. [21]. As in the case of DHIQ, the apparent lack of correlation between the α parameter of the NEF is likely to be sought in the presence of a strong secondary relaxation, intramolecular in nature, as detected by standard spectroscopic techniques such as DRS [24]. Dalle-Ferrier et al. [**?**] investigated the molecular weight dependence of the correlation α p arameter of the NEF in polystyrene (PS) and poly(iso butylene) (PIB). They found that the correlation fragility *versus* α is lost once PS molecular weight is increased and that of PIB decreased. In the former case, it is interesting to recall a recent study on the dependence on the molecular weight of PS molecular dynamics [10]. This shows that high molecular weight PS exhibits pronounced secondary relaxation, whereas such process tends to disappear when lowering the molecular weight. At molecular weights smaller than 700 Kg mol^{-1} no secondary relaxations can be detected. This result is a further strong indication of the need to properly determine the NEF in large molecular weight PS(s) for a meaningful comparison with the fragility. In the case of PIB, an opposite scenario exists: low molecular weight PIB exhibits significant deviations from the expected correlation of m and α. Unfortunately systematic studies on the relaxation behavior of PIB as a functi on of the molecular weight have not been performed in the past. In particular, the presence of secondary relaxations in this polymer and whether such relaxations exist over the whole range of molecular weights should be explored for a correct interpretation of *m verus* α results.

Summing up, whatever the approach followed for the description of the fragility is, a detailed analysis of the global properties of the glass former under examination should be pursued. In particular, a straightforward comparison between properties representative of the overall nature of the glass formers and fragility, under the strong assumption of a single process, the structural relaxation, is not always possible. In this contribution the effect of secondary relaxations to the overall excess entropy and NEF has been emphasized.

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Reprint 16-1: Is the Fragility of a Liquid Embedded in the Properties of its Glass

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T. Scopigno, G. Ruocco, F. Sette and G. Monaco

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the GB that were not considered in the theoretical studies. The presence of oxygen vacancies would remove negative charge from the area between the close Ti atom columns and thus increase the Ti-Ti distance, as found in our experiment.

We have shown how HRTEM can be used for direct imaging of the oxygen sublattice near a crystal defect in $SrTiO_3$ at atomic resolution. In addition to this structural information, a quantitative comparison with simulated HRTEM images should enable determination of the local chemical composition of oxides on the atomic scale. Our results strongly indicate that it should also be possible to resolve light elements in nonoxide materials such as borides, nitrides, or carbides. This would be of central importance for the understanding of defects in these materials.

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11. The experimental image presented here was obtained from digital charge-coupled device camera recordings of the original negative films. It can grab image pixels from an area of 1536 × 1024 pixels at a spatial sampling rate of 0.013 nm/pixel. The displacement analysis was done in the negative image with DigitalMicrograph 3.6 (Gatan).
12. For δ_i^T and δ_i^S we only measured the spacing in the upper crystal because the contrast is more homogeneous in this part of the image. For δ_i^C we measured spacings from both the upper and lower crystals. The error bars correspond to the standard deviation determined from the statistical average.
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Is the Fragility of a Liquid Embedded in the Properties of Its Glass?

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When a liquid is cooled below its melting temperature, it usually crystallizes. However, if the quenching rate is fast enough, the system may remain in a disordered state, progressively losing its fluidity upon further cooling. When the time needed for the rearrangement of the local atomic structure reaches approximately 100 seconds, the system becomes "solid" for any practical purpose, and this defines the glass transition temperature T_g. Approaching this transition from the liquid side, different systems show qualitatively different temperature dependencies of the viscosity, and accordingly they have been classified by introducing the concept of "fragility." We report experimental observations that relate the microscopic properties of the glassy phase to the fragility. We find that the vibrational properties of the glass well below T_g are correlated with the fragility value. Consequently, we extend the fragility concept to the glassy state and indicate how to determine the fragility uniquely from glass properties well below T_g.

When a liquid is cooled, the loss of kinetic energy leads to an ordering of the molecules, which then crystallize at the melting temperature T_m. However, if cooled fast enough through T_m, some materials (glass-forming materials) are capable of sustaining a metastable liquid state and, upon further cooling, of freezing into a disordered glassy state (*1*–*4*). The law that describes the change of the viscosity with the temperature approaching the glass transition temperature, T_g, is highly material-specific and has led to the classification of glass-forming materials according to the concept of "fragility" (*5*, *6*). The kinetic fragility, m, is directly related to the slowing down of the dynamics: It is defined in terms of the shear viscosity η as

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

Therefore, m is an index of how fast the viscosity increases while approaching the structural arrest at T_g, the temperature at which the structural relaxation time $\tau_\alpha \sim 100$ s. At this latter temperature, through the Maxwell relation $\eta = G_\infty \tau$, one finds a viscosity of $\eta \sim 10^{13}$ poise (more likely, $\eta \sim 10^{11}$ poise for molecular glasses), whereas 10^{-4} poise is the "infinite" temperature limit in basically any material. Consequently, fragility values typically range between $m = 17$ for "strong" systems (those that show an Arrhenius behavior) and $m \sim 150$ for "fragile" systems, where the high cooperativity of the diffusive dynamics induces a high (and T-dependent) apparent activation energy. One interesting element of this classification lies in the attempt to relate the temperature behavior of a macroscopic transport property close to T_g to the microscopic interactions driving the dynamics of the system. It has been found, for example, that the value of the fragility is empirically related to the kind of interaction potential among the particles constituting the system. Prototypical examples of fragile liquids are those composed by units interacting via isotropic bonds, such as van der Waals–like molecular liquids. The strong glass-forming liquids, on the other hand, are those characterized by strong covalent directional bonds that form space-filling networks. *O*-terphenyl ($m = 80$) and SiO_2 ($m = 20$) are characteristic examples of a fragile and a strong liquid, respectively. Hydrogen-bonded systems, such as glycerol ($m = 50$), are often called "intermediate" between strong and fragile liquids. Kinetic fragility has been found to be correlated to other properties of the glass-forming liquids, such as (i) the slope at T_g of the temperature dependence of the configurational entropy (often referred to as thermodynamic fragility) (*7*) or (for classes of systems sharing similar T_g's) the specific heat jump at T_g (*8*, *9*); (ii) the ratio between the maximum and the minimum of the boson peak; that is, of the bump observed at terahertz frequencies in the Raman and neutron-scattering spectra of glass-forming materials (*10*) [although this finding is controversial (*11*)]; (iii) the degree of stretching in the nonexponential decay of the correlation functions in the liquid close to T_g (*12*); (iv) the statistics of the minima in a potential energy landscape–based description (*13*, *14*) of the diffusion process in supercooled liquids (*15*–*17*); and, more recently, (v) the temperature behavior of the shear elastic modulus in the supercooled liquid (*18*). In all these studies, the fragility has been always related to (or defined through) macroscopic properties characterizing the liquid side of the glass transition. Although there are attempts to relate the fragility to the anharmonicity of the "hot" glass (*19*), no connection has been found up to now between the

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value of *m* and the physical properties of the low-temperature glassy phase.

We show that, starting from a determination of the nonergodicity factor in the low-temperature glass, it is possible to identify a parameter that controls how fast the nonergodicity factor decreases when the temperature is increased, and that turns out to be proportional to the fragility *m*. Through this, we establish a way to determine the fragility of a system in the glassy phase well below T_g, independent of the way in which viscosity changes with decreasing temperature from the liquid side. By exploiting the harmonic approximation of the low-temperature dynamics, it is found that this parameter only depends on the characteristics of the static disorder, which in turn controls the vibrational eigenmodes of the glass. This result demonstrates the existence of a deep link between the diffusive interbasin dynamics and the vibrational intrabasin dynamics in glass-forming systems.

Recent extensive inelastic x-ray scattering (IXS) measurements of the dynamic structure factor have allowed a sizeable library of high-frequency (terahertz) dynamical properties of glasses to be constituted. Of interest here is the fact that the IXS measurements allow for the determination of the nonergodicity factor $f(Q,T)$, with a reliability that was not achievable via light or neutron scattering (*20*). The nonergodicity factor is the long time limit of the density correlator $\Phi_Q(t)$; that is, the density-density correlation function $F(Q,t)$, normalized to the static structure factor $S(Q)$: $\Phi_Q(t) = F(Q,t)/S(Q)$. The quantity $1 - f(Q,T)$ represents the amount of decorrelation introduced by the vibrational dynamics, and it depends on both the (T-dependent) amplitude of the vibrations and the degree of disorder of the glassy structure. In a low-temperature glass, $F(Q,t)$, apart from the Debye-Waller factor $\exp[-W(Q)]$, can be expressed as the sum of a constant term $S_{IS}(Q)$, which represents the static structure factor of the atomic equilibrium positions (inherent structure), plus a time-dependent one, $F_{inel}(Q,t)$, which is the contribution of the atomic vibration around such equilibrium positions, a quantity that vanishes in the long time limit

$$F(Q,T) = e^{-W(Q)}[S_{IS}(Q) + F_{inel}(Q,t)] \quad (1)$$

Therefore,

$$f(Q,T) = \lim_{t \to \infty} \Phi_Q(t) =$$

$$\lim_{t \to \infty} \frac{S_{IS}(Q) + F_{inel}(Q,t)}{S_{IS}(Q) + S_{inel}(Q)} = \frac{1}{1 + S_{inel}(Q)/S_{IS}(Q)} \quad (2)$$

where we have defined $S_{inel}(Q) \doteq F_{inel}(Q,t = 0)$. $S(Q,\omega)$ is the Fourier transform of $F(Q,t)$ and is the quantity directly accessible in scattering experiments. From Eq. 1 it can be expressed as

$$S(Q,\omega) = e^{-W(Q)}[S_{IS}(Q)\delta(\omega) + S_{inel}(Q,\omega)] \quad (3)$$

From an experimental point of view and according to Eqs. 2 and 3, the nonergodicity factor is derived from the ratio of the elastic to the inelastic scattered intensity, obtained from inelastic scattering measurements of the dynamic structure factor $S(Q,\omega)$ (*21*). A sense of the T dependence of $f(Q,T)$ can be obtained from Fig. 1. Here, as an example, we report the IXS spectra at fixed exchanged wave vector ($Q = 2$ nm^{-1}) and at different temperatures in glycerol. The inelastic (dashed lines) and elastic (dotted

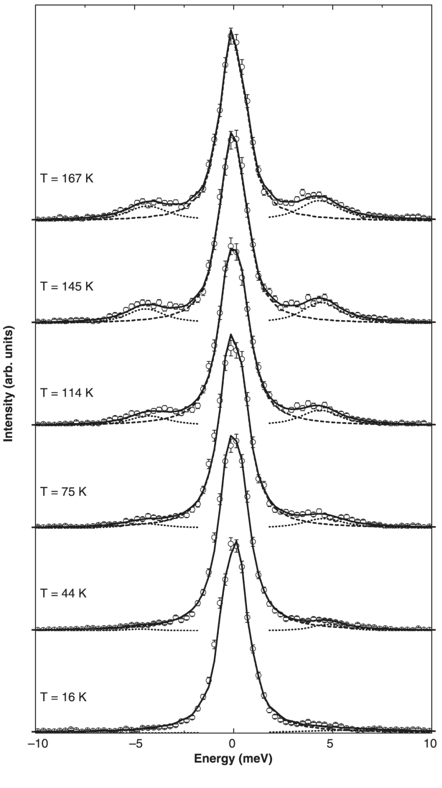


Fig. 1. Selected example of the inalastic x-ray scattering energy spectra of glycerol (open circles with error bars) taken at $Q = 2$ nm^{-1} at the indicated temperatures. The solid line is the line of best fit according to Eq. 3 and eq. S2, whereas the dashed and dotted lines are the elastic and inelastic contributions, respectively (see the supporting online material for further details). The values of $f(Q,T)$ are obtained by the ratio of the integrated intensities of the elastic and inelastic contribution, from Eq. 2. arb., arbitrary.

Table 1. Temperature steepness of the viscosity at T_g (fragility) and of the nonergodicity factor at $T \rightarrow 0$ (α) for several materials.

Sample	T_g (K)	m	α
BeF_2*	598	20	0.16
Silica†	1450	28	0.19
Glycerol‡	190	53	0.32
$PB_{1,4}$§	180	60	0.40
nBB‖	125	53	0.46
Salol¶	218	73	0.64
mtol#	187	77	0.57
oTP**	241	81	0.58
mTCP††	205	87	0.59
Se‡‡	308	87	0.7

*m from (*26*), α from (*27*). †Silica infrasil-grade sample. m from (*12*), α from (*28*) and references therein. ‡m from (*12*), α from (*29*). §Polybutadiene: α is determined from an experiment performed on a sample constituted of 1.4 structural units only, reported in (*30*). The fragility is not directly available for such a composition; we estimated m by extrapolating data for several concentrations of mixtures composed of 1.2 and 1.4 structural units, available from (*12*, *31*). ‖Normal butyl-benzene: m from (*32*), α from the experiment in (*33*). ¶m from (*12*), α from unpublished data. #Metatoluidine: m from (*34*), α from unpublished data. **O-terphenyl: m from (*12*), α from (*35*). ††Metatricresylphosphate: m from (*12*), α from unpublished data. ‡‡m from (*12*), α from unpublished data.

lines) contributions to the scattering intensity are shown, and one can appreciate in the raw data the change of relative intensity as a function of T. As far as the Q dependence is concerned, $f(Q,T)$ follows in phase the oscillations of the static structure factor and is almost Q-independent in the $Q \to 0$ region, where $S(Q)$ is almost constant (*22*), (see the inset of Fig. 2). We focus on this small-Q region. From the integrated intensities of the elastic and inelastic contributions, obtained by a fitting procedure (see eqs. S1 and S2 of the supporting on line material), the T dependence of $f(Q,T)$ is obtained. The values of $f(Q,T)^{-1}$ (which is expected to be linear in T) are reported in Fig. 2 (triangles). Also reported in the same figure is the T dependence of $f(Q,T)$ for two other archetypical glasses: silica and O-terphenyl (oTP).

To better understand the temperature dependence of $f(Q,T)$ in the $T \to 0$ limit, we invoke the harmonic approximation for the vibrational dynamics. This allows one to express $f(Q,T)$ in terms of the vibrational properties of the systems; that is , the eigenvalues (ω_p) and eigenvectors ($\bar{e}_p$) of the potential energy Hessian, evaluated at the inherent structure. Using the harmonic approximation for $S_{\mathrm{inel}}(Q,\omega)$, it is straightforward (*23*, *24*) to show that Eq. 2 reduces to

$$f(Q,T)=\left[1+\frac{K_{\mathrm{B}}TQ^2}{MS_{\mathrm{IS}}(Q)}\frac{1}{N}\sum_p\frac{\left|\Sigma_i[\hat{Q}\cdot\bar{e}_p(i)]e^{iQr_i}\right|^2}{\omega_p^2}\right]^{-1} \tag{4}$$

Here M is the molecular mass, K_{B} is the Boltzmann constant, and i is summed over the N particles and p over the $3N$ normal modes. In order to pinpoint the T dependence of the nonergodicity factor in the low Q limit, it is convenient to rewrite Eq. 4 as

$$f(Q\to 0,T)=\frac{1}{1+\alpha\frac{T}{T_{\mathrm{g}}}} \tag{5}$$

We thus define the dimensionless quantity α, which encompasses all the microscopic details of the system, as the eigenvalues and eigenvectors of the normal modes. These are quantities that, in turn, depend on the interaction potential and on the disordered structure. This equation provides a formal way to extract the system-dependent parameter α from the T dependence of $f(Q,T)$, derived from the IXS data. This has motivated us to revisit the large amount of IXS data available for glasses at low T, where the harmonic approximation, and therefore Eq. 5, is expected to be valid. As it can be seen in Fig. 2, the observed T dependence of $f(Q,T)$ is fully consistent with the functional form predicted by Eq. 5, and this allows us to determine α by a least-squares minimization procedure. The derived values for α (such as $\alpha = 0.19$ for silica, $\alpha = 0.32$ for glycerol, and $\alpha = 0.58$ for oTP) clearly indicate a trend: The more fragile a liquid, the greater the slope of $f(Q,T)$ at $T = 0$; that is, the faster the decorrelation of the density fluctuations on increasing T. The fitting procedure has been applied to the whole set of available glasses, and the obtained values of α are reported in Table 1 and Fig. 3 as a function of the independently known fragility parameter m. Figure 3 clearly shows the existence of a strong correlation between m and α: The higher the fragility, the higher the value of α; that is, the faster is the T dependence of the $f(Q,T)$ parameter. The existence of a strong correlation between α and m is further emphasized by the empirical observation that the two quantities are not only correlated but (within the statistical accuracy) are actually proportional to each other, according to the relation $m = (135 \pm 10)\alpha$. In passing, we note that the two points that lie definitely below the dotted line (selenium and salol) are the ones for which fragility determined at T_{g} doesn't agree well with the fragilities determined at higher temperatures (*7*, *25*).

Fig. 2. Values of $f(Q^*,T)^{-1}$ (Eq. 2) for $Q^* \cong 2$ nm^{-1} reported in a T/T_{g} scale for three representative materials (solid symbols with error bars): silica ($T_{\mathrm{g}} = 1450$ K), glycerol ($T_{\mathrm{g}} = 190$ K), and oTP ($T_{\mathrm{g}} = 241$ K). The full line is the best fit of the experimental data to Eq. 5. These fits have been used to derive the values of α reported in Fig. 3. The inset shows the Q dependence of $f(Q,T^*)$ for silica at $T^* = 1050$ K.

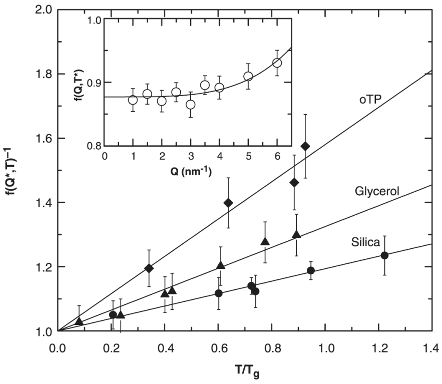
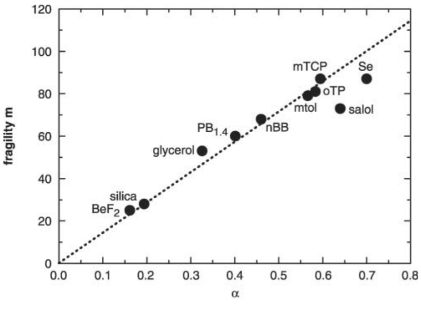


Fig. 3. Correlation plot of the kinetic fragility and the α parameter of the nonergodicity factor (Eq. 5). The dotted line is obtained by a fit of the data to a linear equation. It corresponds to $m = 135\alpha$, and the regression coefficient is $r = 0.994$.



The observed correlation is conceptually surprising. It indicates the existence of a link between the curvatures of the potential energy function at its minima (more specifically, those visited in the glassy phase) and the other properties of the potential energy function (the energy distribution of the minima, minimum-to-minimum barrier height, distribution of the saddle order and energies, etc.) controlling the diffusive processes in supercooled liquids.

We further examine how α emerges from the collective density-density correlation function plateau. From Eqs. 4 and 5, the microscopic expression for α is found to be

$$\alpha=\left[\frac{K_{\mathrm{B}}T_{\mathrm{g}}Q^2}{MS_{\mathrm{IS}}(Q)}\frac{1}{N}\sum_p\frac{\left|\Sigma_i[\hat{Q}\cdot\bar{e}_p(i)]e^{iQr_i}\right|^2}{\omega_p^2}\right]^{-1} \tag{6}$$

One may in principle derive a similar parameter α_{s} from the temperature dependence of the self-correlator plateau. In this case, α_{s} is related to the familiar mean square displacement.

The harmonic approximation for theDebye-Waller factor $f_s(Q,T) = \exp[-W(Q,T)]$ would lead to an equation formally identical to Eq. 5, but with α replaced by α_{s}

$$\alpha_s = \left[\frac{K_B T_g Q^2}{M}\frac{1}{N}\sum_p \frac{1}{\omega_p^2}\right]^{-1} \qquad (7)$$

Therefore α and α_s differently weight the low-frequency modes. Specifically, in the small Q limit, α is more sensitive to the low-energy modes than α_s, which, independently of Q, reflects the whole density of states. It would be interesting to investigate whether these two quantities are correlated with each other.

Here we report evidence for correlation between the fragility of a glass-forming liquid and the temperature dependence of its nonergodicity factor, as determined by the vibrational dynamics at very low temperatures. The fragility is an index of how the viscosity increases upon supercooling. The nonergodicity factor, in the low temperature limit, is related to the vibrational properties of the harmonic glassy dynamics (Eq. 6); that is, to the curvature of the energy minima. Therefore, from our finding it emerges that the properties of the potential energy landscape around the deep minima are related to those properties that control the diffusion of the system through different basins. This unexpected relation is a further aspect of the physics of the glass transition that needs to be clarified.

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Methods
References

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Decadal Variation of the Surface Water $P\text{CO}_2$ in the Western and Central Equatorial Pacific

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The equatorial Pacific Ocean is one of the most important yet highly variable oceanic source areas for atmospheric carbon dioxide (CO_2). Here, we used the partial pressure of CO_2 ($P\text{CO}_2$), measured in surface waters from 1979 through early 2001, to examine the effect on the equatorial Pacific CO_2 chemistry of the Pacific Decadal Oscillation phase shift, which occurred around 1988 to 1992. During the decade before the shift, the surface water $P\text{CO}_2$ (corrected for temperature changes and atmospheric CO_2 uptake) in the central and western equatorial Pacific decreased at a mean rate of about –20 μatm per decade, whereas after the shift, it increased at about +15 μatm per decade. These changes altered the CO_2 sink and source flux of the equatorial Pacific significantly.

The equatorial Pacific Ocean is known to undergo significant changes on interannual time scales (e.g., El Niño and La Niña) and on decadal time scales. This area is a major source of CO_2 to the atmosphere during non–El Niño periods (*1–5*) but near neutral during strong El Niño periods (*2–5*). Over decadal time scales, the North Pacific Ocean has undergone major physical and biological changes commonly called the Pacific Decadal Oscillation (PDO) (*6–9*). The most recent and major shifts of 1977 and 1988 to 1992 have been documented on the basis of extensive physical and biological information (*6–8*). Although the causes and effects of PDO have been investigated in recent years, its effects on CO_2 chemistry have not yet been identified. Here, we describe the changes in CO_2 chemistry in the Pacific equatorial waters associated with the 1988 to 1992 PDO phase shift (*6–8*) using the partial pressure of CO_2 ($P\text{CO}_2$) in seawater, which is a measure of the escaping tendency of CO_2 from seawater to the overlying atmosphere.

Because of the heightened interest in the El Niño–Southern Oscillation (ENSO) events and the carbon cycle, $P\text{CO}_2$ in surface ocean waters has been measured more frequently since 1979 over the equatorial Pacific Ocean. In this study, we assembled a database containing about 100,000 $P\text{CO}_2$ observations made in surface waters of the equatorial belt, 5°N to 5°S, between April 1979 and March 2001 (*10*). We classified these into three groups: (i) the Niño 3.4 area (lat 5°S to 5°N, long 170°W to 120°W) during non–El Niño periods (which include La Niña periods); (ii) the Niño 3.4 area during El Niño periods; and (iii) the western warm pool area (lat 5°N to 5°S, long 175°E to 135°E). We identified six El Niño periods in the Niño 3.4 area on the basis of sea surface temperature (SST) anomalies (*11*). The remaining data were considered as occurring during non–El Niño periods.

In the Niño 3.4 area, observations during non–El Niño periods were made more or less evenly throughout the year along a total of 11 meridional transects across the equator during the pre-1990 period, and 14 transects during the post-1990 period. In this area, no measurements

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Reprint 16-2: Universal Relation between Viscous Flow and Fast Dynamics in Glass-forming Materials

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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.

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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 α 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]

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

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:

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

and, most important, (iii) a direct proportionality

$$m \propto \alpha \tag{3}$$

(with a proportionality factor ≈ 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

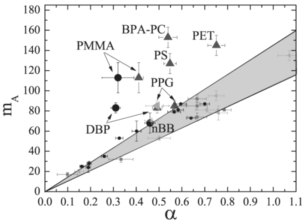

FIG. 1. (Color online) Correlation between the temperature dependencies of relaxation time (fragility, m) and NEF (α). This latter was determined assuming that a single (structural) relaxation governs the microscopic dynamics using: IXS [black circles, in order of increasing fragility: NiZr, BeF_2, Silica, 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_2O_3, B_2O_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 α 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) evaluating the sound velocity jump at the glass transition temperature $c_{liquid}(T \rightarrow T_g^+)/c_{glass}(T \rightarrow T_g^-) = c_0(T_g)/c_\infty(T_g)$ by means of Brillouin light scattering and ultrasonics (green symbols) or compressibility (χ) measurements (blue symbols) via the expression:[22]

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

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 β) 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) α as

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

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

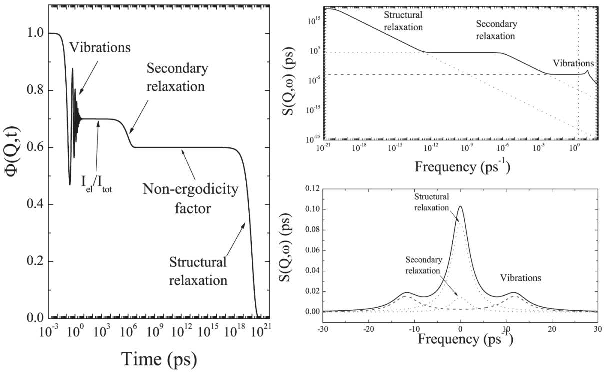

FIG. 2. (Color online) Toy model illustrating how the presence of a secondary relaxation affects the DAF. Left panel: DAF in presence of an additional "slow" relaxation. Right upper panel: the corresponding DSF (black line). Vibrational contribution (dashed blue line) and structural and secondary relaxations (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 α 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 α parameter.[39]

This observation can explain, for instance, the scattering of the points of m-α 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 (Σ_{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, Σ_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

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

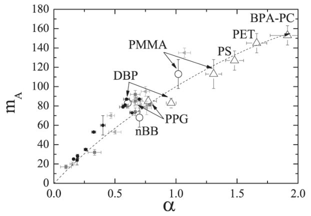

FIG. 3. (Color online) Correlation between the temperature dependencies of relaxation time (fragility, m) and NEF (α) accounting for the presence of secondary relaxations. The α parameter was indeed corrected through Eqs. (5) and (10) for all polymers possessing secondary relaxation processes plus DPB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

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 α relaxation-related excess entropy should be left out, the residual excess entropy at T_0 has been attributed to non-α 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-α 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 α 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 nonergodicity 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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