Is the Fragility of a Liquid Embedded in the Properties of its Glass?

Tullio Scopigno, Giancarlo Ruocco, Francesco Sette, Giulio Monaco

1INFM and Dipartimento di Fisica, Universitá di Roma La Sapienza, 00185 Roma, Italy,
2European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France
*To whom correspondence should be addressed; E-mail: tullio.scopigno@phys.uniroma1.it

When a liquid is cooled below its melting temperature it usually crystallizes. However, if the quenching rate is fast enough, it is possible that the system remains 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 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
some materials (glass forming materials) are capable to sustain a metastable liquid state and, upon further cooling, to freeze into a disordered glassy state \( T_m \). 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 the glass formers materials according to the concept of "fragility" \( \xi, 2, 3, 4 \). The kinetic fragility, \( m \), is directly related to the slowing down of the dynamics: it is defined in terms of the shear viscosity \( \eta \) 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 approaching the structural arrest at the glass transition temperature \( T_g \), the temperature where the structural relaxation time \( \tau_\alpha \sim 100 \text{ s} \). At this latter temperature, through the Maxwell relation \( \eta = G_\infty \tau_\alpha \), corresponds a viscosity \( \eta \sim 10^{13} \) poise (more likely \( \eta \sim 10^{11} \) poise for molecular glasses), while \( 10^{-4} \) poise is the "infinite" temperature limit in basically any materials. Consequently, fragility values typically range between \( m = 17 \) for "strong" systems -those that show an Arrhenius behaviour- 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 interest in 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, as glycerol \( (m=50) \), are often called "intermediate" between strong and fragile liquids.
netic 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 glass transition temperatures- the specific heat jump at $T_g$ (8, 9); ii) the ratio between the maximum and the minimum of the boson peak, i.e. of the bump observed at the THz in the Raman and neutron scattering spectra of glass-forming materials (10), but this finding is controversial (11); iii) the degree of stretching in the non-exponential 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, 16, 17), and, more recently, v) the temperature behaviour 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. While 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 value of $m$ and the physical properties of the low temperature glassy phase.

We show that, starting from a determination of the non ergodicity factor in the low temperature glass, it is possible to identify a parameter that controls how fast the non ergodicity factor decreases on increasing the temperature, 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 the 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 inter-basins dynamics and the vibrational intra-basin dynamics.

Recent extensive inelastic x-ray scattering (IXS) measurements of the dynamic structure
factor have allowed to constitute a sizeable library of high frequency (THz) dynamical properties of glasses. Of interest here, the IXS measurements allow for the determination of the non-ergodicity factor, \( f(Q, T) \) with a reliability that was not achievable via light or neutron scattering \(^2\). The non ergodicity factor is the long time limit of the density correlator, \( \Phi_Q(t) \), i. e. 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 represent 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:

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

(1)

Therefore:

\[
f(Q, T) = \lim_{t \to \infty} \Phi_Q(t) = \lim_{t \to \infty} \frac{S_{IS}(Q) + F_{inel}(Q, t)}{S_{IS}(Q) + S_{inel}(Q)} = \frac{1}{1 + S_{inel}(Q)/S_{IS}(Q)}
\]

(2)

where we have defined \( S_{inel}(Q) \equiv F_{inel}(Q, t = 0) \). \( S(Q, \omega) \) 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

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

(3)

From an experimental point of view and according to Eqs (2) and (3), the non ergodicity
factor is derived from the ratio of the elastic to the inelastic scattered intensity, obtained from inelastic scattering measurements of the dynamic structure factor $S(Q, \omega)$ \cite{27}. 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 wavevector ($Q = 2 \text{ nm}^{-1}$) and at different temperatures in glycerol. The inelastic (dashed lines) and elastic (dotted 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 \cite{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 Eq. (S1) and (S2) of the supporting on line materials), the $T$ dependence of $f(Q, T)$ is obtained. The values of $f(Q, T)^{-1}$ (which is expected to be linear in $T$, see below) 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, i.e. the eigenvalues ($\omega_p$) and eigenvectors ($\vec{e}_p$) of the potential energy Hessian evaluated at the inherent structure. Using the harmonic approximation for $S_{inel}(Q, \omega)$, it is straightforward \cite{23,24} to show that Eq. (2) reduces to:

$$f(Q, T) = \left[ 1 + \frac{K_B T Q^2}{MS_{IS}(Q)} \sum_p \frac{\left| \sum_i (Q \cdot e_p(i)) e^{iQr_i} \right|^2}{\omega_p^2} \right]^{-1}. \quad (4)$$

Here $M$ is the molecular mass, $K_B$ 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
\[ f(Q \rightarrow 0, T) = \frac{1}{1 + \alpha \frac{T}{T_g}}. \]  

(5)

We thus define the dimensionless quantity \( \alpha \), 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 \( \alpha \) 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 \( \alpha \) by a least square minimization procedure. The derived values for \( \alpha \) (e. g. \( \alpha = 0.19 \) 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 \( T = 0 \), i. e. 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 \( \alpha \) are reported in Tab.I and Fig. 3 as a function of the independently known fragility parameter \( m \). From this figure clearly emerges the existence of a strong correlation between \( m \) and \( \alpha \): the higher the fragility, the higher the value of \( \alpha \), i. e. the faster is the \( T \) dependence of the \( f(Q, T) \) parameter. The existence of a strong correlation between \( \alpha \) and \( m \) is further emphasized by the empirical observation that the two quantities are not only correlated but (within the statistical accuracy) actually proportional to each other, according to the relation \( m = (135 \pm 10)\alpha + (4 \pm 5) \). On 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).

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 (energy distribution of the minima, minimum-to-minimum barrier height, distribution of the saddle order and energies,...) controlling the diffusive processes in supercooled liquids.

We further examine how $\alpha$ emerges from the collective density-density correlation function plateau. From Eqs. (4) and (5), the microscopic expression for $\alpha$ is found to be:

$$\alpha = \frac{K_B T_g Q^2}{M S_{1S}(Q)} \frac{1}{N} \sum_p \left| \sum_i \left[ \hat{Q} \cdot e_p(i) \right] e^{iQr_i} \right|^2$$  \hspace{1cm} (6)

One may in principle derive a similar parameter $\alpha_s$ from the temperature dependence of the self correlator plateau. In this case $\alpha_s$ is related to the familiar mean square displacement. The harmonic approximation for the Debye Waller factor $f_s(Q, T) = \exp (-W(Q, T))$ would lead to an equation formally identical to Eq.(5), but with $\alpha$ replaced by $\alpha_s$:

$$\alpha_s = \frac{K_B T_g Q^2}{M} \frac{1}{N} \sum_p \frac{1}{\omega_p^2}$$  \hspace{1cm} (7)

Therefore $\alpha$ and $\alpha_s$ differently weight the low frequency modes. Specifically, in the small $Q$ limit, $\alpha$ is more sensitive to the low energy modes than $\alpha_s$ that, independently on $Q$, reflects the whole density of states. It would be interesting to check whether or not these two quantities are correlated with each other.

In conclusion, we report evidence for the correlation between the fragility of a glass-forming liquid and the temperature dependence of its non-ergodicity factor as determined by the vibrational dynamics at very low temperatures. The fragility is an index of how the viscosity increases upon supercooling. The non-ergodicity factor, in the low temperature limit, is related to the vibrational properties of the harmonic glassy dynamics (see Eq.(6)), i.e. 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 diffu-
sion of the system through different basins. This unexpected relation represents a further aspect that requires to be clarified in the physics of the glass-transition.
Table 1: Temperature steepness of the viscosity at $T_g$ (fragility) and of the non ergodicity factor at $T \to 0$ ($\alpha$) for several materials.

| Sample     | $T_g$ [K] | $m$  | $\alpha$ |
|------------|-----------|------|----------|
| 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      |

\(^a\)m from Ref. (26), $\alpha$ from Ref. (27).
\(^b\)Silica infrasil grade sample. $m$ from Ref. (12), $\alpha$ from Ref. (28) and references therein.
\(^c\)m from Ref. (12), $\alpha$ from Ref. (29).
\(^d\)Polybutadiene: $\alpha$ is determined from an experiment performed on a (1.2PBD)$_0$(1.4PBD)$_{100}$ reported in Ref. (30). The fragility is not available for such concentration, we estimated $m$ extrapolating data from Refs. (27, 12).
\(^e\)Normal-butyl-benzene: $m$ from Ref. (32), $\alpha$ from the experiment in Ref. (33).
\(^f\)m from Ref. (12), $\alpha$ from unpublished data.
\(^g\)Meta-toluidine: $m$ from Ref. (34), $\alpha$ from unpublished data.
\(^h\)Orto-terphenyl: $m$ from Ref. (12), $\alpha$ from Ref. (35).
\(^i\)Meta-tricresyl-phosphate: $m$ from Ref. (12), $\alpha$ from unpublished data.
\(^j\)m from Ref. (12), $\alpha$ from unpublished data.
References and Notes

1. K. Ngai, ed., *Proc. of the 4th International Discussion Meeting on Relaxations in Complex Systems*, vol. 307-319 (2002). Special Issues of the Journal of Non-Crystalline Solids.

2. M. Giordano, D. Leporini, M. Tosi, eds., *Articles presented at the Second International Workshop on Non-Equilibrium Phenomena in Supercooled Fluids, Glasses and Amorphous Materials*, vol. 11 (1999). Special issue of the Journal of Physics, Condensed Matter.

3. L. Andreozzi, M. Giordano, D. Leporini, M. Tosi, eds., *Articles presented at the Third International Workshop on Non-Equilibrium Phenomena in Supercooled Fluids, Glasses and Amorphous Materials*, vol. 15 (2003). Special issue of the Journal of Physics, Condensed Matter.

4. P. G. Debenedetti, F. H. Stillinger, *Nature* **410**, 259 (2001).

5. C. A. Angell, *J. Non-Cryst. Solids* **131-133**, 13 (1991).

6. C. A. Angell, *Science* **267**, 1924 (1995).

7. L.-M. Martinez, C. A. Angell, *Nature* **410**, 663 (2001).

8. D. Huang, G. McKenna, *J. Chem. Phys.* **13**, 5621 (2001).

9. K. Ngai, O. Yamamuro, *J. Chem. Phys.* **23**, 10403 (1999).

10. A. Sokolov, E. Rössler, A. Kisliuk, D. Quittman, *Phys. Rev. Lett.* **71**, 2062 (1993).

11. S. Yannopoulos, G. Papatheodorou, *Phys. Rev. E* **62**, 3728 (2000).

12. R. Böhmert, K. L. Ngai, C. A. Angell, D. J. Plazek, *J. Chem. Phys.* **99**, 4201 (1993).

13. M. Goldstein, *J. Chem. Phys.* **51**, 3728 (1969).
14. W. H. Stillinger, T. A. Weber, *Phys. Rev. A* **25**, 978 (1982).

15. R. Hall, P. Wolynes, *J. Chem. Phys.* **86**, 2943 (1987).

16. R. J. Speedy, *J. Phys. Chem. B* **103**, 4060 (1999).

17. S. Sastry, *Nature* **409**, 164 (2001).

18. J. C. Dyre, N. Olsen, cond-mat/0211042 **409**, 164 (2001).

19. F. Mallamace, H. E. Stanley, eds., *Proc. Int. School of Physics Enrico Fermi, Course CXXXIV*, vol. 11 (1997). The Glassy State Problem: Failure to Crystallize, and Vitrification, C.A. Angell.

20. F. Sette, M. Krisch, C. Masciovecchio, G. Ruocco, G. Monaco, *Science* **280**, 1550 (1998).

21. Some fraction of the elastic line may be in principle related to the non-propagating temperature fluctuations. The amount of this contribution is actually ruled out by the quantity \( \frac{c_p}{c_v} - 1 = \gamma - 1 \) and therefore it vanishes in the \( T \to 0 \) limit when \( \gamma \to 1 \) holds according to the harmonic approximation.

22. A. Tölle, H. Schober, J. Wuttke, F. Fujara, *Phys. Rev. E* **56**, 809 (1997).

23. G. Ruocco, *et al.*, *Phys. Rev. Lett.* **84**, 5788 (2000).

24. T. Scopigno, G. Ruocco, F. Sette, G. Viliani, *Phys. Rev. E* **66**, 031205 (2002).

25. J. Garrahan, D. Chandler, *Proc. Natl. Acad. Sci.* **100**, 9710 (2003).

26. M. Hemmati, C. T. Moynihan, C. A. Angell, *J. Chem. Phys.* **115**, 6663 (2001).

27. T. Scopigno, *et al.*, *J. Chem. Phys.* **118**, 311 (2003).

28. C. Masciovecchio, *et al.*, *Phys. Mag. B* **79**, 2013 (1999).
29. G. Ruocco, et al., *Phys. Rev. Lett.* **83**, 5583 (1999).

30. D. Fioretto, et al., *Phys. Rev. E* **59**, 4470 (1999).

31. R. Zorn, G. B. McKenna, L. Willner, D. Richter, *Macromolecules* **28**, 8552 (1995).

32. C. Hansen, F. Stickel, R. Richert, E. W. Fisher, *J. Chem. Phys.* **108**, 6408 (1998).

33. C. Masciovecchio, et al., *Phys. Rev. Lett.* **80**, 544 (1998).

34. B. M. Erwin, R. H. Colby, *J. Non-Cryst. Solids* **307-310**, 225 (2002).

35. G. Monaco, C. Masciovecchio, G. Ruocco, F. Sette, *Phys. Rev. Lett.* **80**, 2161 (1998).

36. The authors gratefully acknowledge C.A. Angell for valuable hints and suggestions. J. Dyre, S. Sastry, F. Sciortino and S. Yannopoulos are also acknowledged for fruitful discussions.
Figure 1: Selected example of the inelastic 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 Eqs (3) and (S2), while the dashed and dotted lines are the elastic and inelastic contributions, respectively (see the supporting on line 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).
Figure 2: Values of $f(Q^*, T)^{-1}$ (Eq. (2)) for $Q^* \approx 2$ nm$^{-1}$ reported in a $T/T_g$ scale for three representative materials (full symbols with error bars): silica ($T_g=1450$ K), glycerol ($T_g=190$ K) and oTP ($T_g=241$ K). The full line is the best fit of the experimental data to Eqs (5). These fits have been used to derive the values of $\alpha$ reported in Fig. 3. In the inset we show the $Q$—dependence of $f(Q, T^*)$ for Silica at $T^* = 1050$ K.
Figure 3: Correlation plot of the kinetic fragility and the $\alpha$ parameter of the non-ergodicity factor (see 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 $r=0.994$. 