

In **Figure 2a**, we compare the rotational relaxation rate obtained by SRPAC to the sum of the rotational and translational relaxation rates obtained by NFS and Mössbauer Spectroscopy (MS) [1]. Below 190 K the data sets coincide, which means that translational dynamics is absent in the experimental time window. Above 190 K the NFS and MS data begin to deviate from the SRPAC data because translational dynamics is activated. From these results the pure translational relaxation rate can be derived.

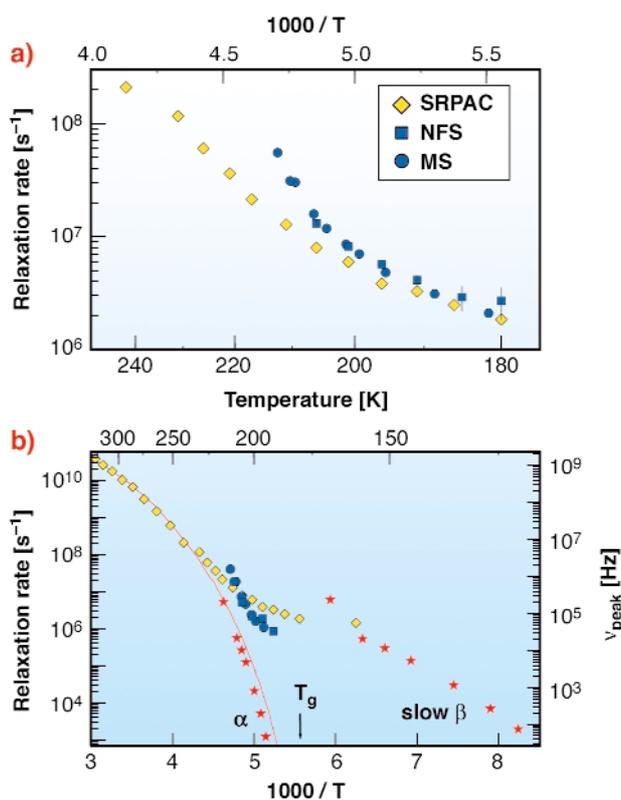


Fig. 2: a) Comparison of the rotational relaxation rate of the ferrocene molecule derived from SRPAC (♦) to the relaxation rate derived from NFS (■) and from Mössbauer spectroscopy (●); b) Comparison of the rotational (♦) and translational (■,●) relaxation rates of the FC molecules to the DS data for pure DBP (red line, ★).

In **Figure 2b** we compare the rotational and translational relaxation rates of the ferrocene molecules in DBP with each other and with data of pure DBP as obtained from dielectric spectroscopy (DS) [2,3]. At low temperatures, the DS data split into two branches. The branch of slow β relaxation follows our data of rotational dynamics, whereas the branch of α relaxation decreases in parallel with our data of translational dynamics. This correlation suggests an interpretation of the ferrocene data also in terms of decoupling, where one branch corresponds to rotational, the other to translational relaxation. In particular, the coincidence of the slow β relaxation branches for probe and solvent suggests that also in pure DBP the slow β relaxation is connected with rotational dynamics.

References

- [1] S.L. Ruby, B.J. Zabransky, P.A. Flinn, *J. Physique* **37**, C6-745 (1976).
- [2] S.A. Dzyuba and Yu.D. Tsvetkov, *J. Struct. Chem.* **28**, 343 (1987).
- [3] P.K. Dixon *et al.*, *Phys. Rev. Lett.* **65**, 1108 (1990).

Principal Publication and Authors

I. Sergueev (a,b), U. van Bürck (a), A.I. Chumakov (b,c), T. Asthalter (d), G.V. Smirnov (c), H. Franz (e), R. Ruffer (b), W. Petry (a), submitted to *Phys. Rev. Lett.*
 (a) TUM Physik E13, Garching (Germany)
 (b) ESRF
 (c) RRC, Moscow (Russia)
 (d) Univ. Stuttgart (Germany)
 (e) DESY, HASYLAB, Hamburg (Germany)

Fragility of Liquids or Fragility of Glasses?

Glasses and the glass transition stand, in the much quoted estimate of a Nobel laureate, as “perhaps the deepest and most interesting unsolved problem in condensed matter physics” [1]. In this respect, one of the most provocative aspects, concerns the slowing down of the dynamics on decreasing the temperature of the melt. When a liquid is cooled, the loss of kinetic energy leads to an ordering of the molecules which ultimately crystallise at the melting temperature T_m . However, if cooled fast enough, some materials (glass forming materials) are capable of sustaining a metastable liquid state and, upon further cooling, to freeze into a disordered glassy state at the glass transition temperature $T_g < T_m$ [2]. Approaching this transition from the liquid side, different systems show qualitatively different temperature dependencies of the viscous flow, commonly represented in the celebrated Angell plot (**Figure 1**). Consequently, on a quantitative ground, liquids have been classified by introducing the

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

term kinetic “fragility” [3]:

A “fragile” liquid shows a fast change in its viscosity, when approaching the glass transition temperature (T_g) and, empirically, it is found that the fragility is related to the interaction potential (Van-der-Waals, hydrogen-bonding, covalent) among the elementary units.

The idea of looking for correlations between fragility and other quantities relevant to the glass transition is not terribly new, its importance was soon recognised as the main road to the understanding of the universality of the Angell plot. But, in the most obvious way, all the efforts have been addressed looking from the liquid side of the glass-transition.

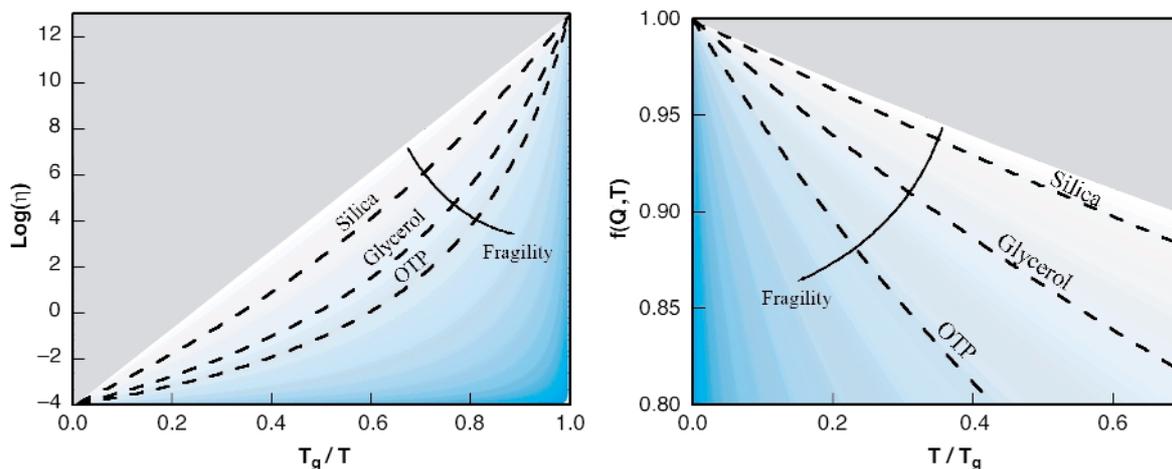


Fig. 1: (Left) kinetic fragility defined as the viscosity derivative at T_g (Angell plot); (Right) glass fragility defined as the derivative of the non-ergodicity factor at $T = 0$. Shaded areas (blue) indicates regions of increasing fragility, gray areas mark regions of unphysical fragilities.

We report here a new experimental observation relating the microscopic properties of the glassy phase to the kinetic fragility. We found that the vibrational properties in the glass away from T_g are correlated to the viscous flow in the liquid on approaching T_g .

Recent Inelastic X-ray Scattering (IXS) measurements of the dynamic structure factor have allowed the constitution of a sizeable library of high-frequency (THz) dynamical properties of glasses. Of interest here, the IXS measurements allow the determination of the non-ergodicity factor, $f(Q,T)$, *i.e.* the long time limit of the normalised density-density correlation function. This quantity 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.

We show that the low temperature dependence of the non ergodicity factor for several glasses stands in a fashion similar to the one exhibited by the Angell plot. It is indeed possible to define a glass fragility as the derivative of $f(Q,T)$ in the $T = 0$ limit (there is almost no Q dependence in the small Q region of interest here) .

$$m_\alpha = \lim_{T \rightarrow 0} \frac{df(Q,T)}{d(T/T_g)}$$

Consequently, we extend the fragility concept to the glassy state and indicate how to determine the fragility uniquely from glass properties far away T_g (Figure 2). More specifically, exploiting the harmonic approximation, one has an analytical dependence of the $f(Q,T)$ which can be used to determine m_α from the experimental data. Through this, we establish a way to determine the fragility of a

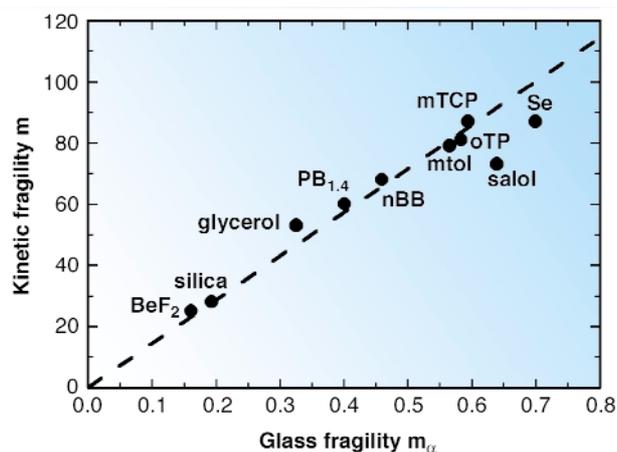


Fig. 2: Correlation of glass and liquid fragilities for an ensemble of glass-formers.

system in the glassy phase well below T_g , independent of the way the viscosity changes with decreasing temperature from the liquid side. This conceptually surprising link between vibrational motion in glasses and diffusive processes in supercooled liquids represents a further aspect that requires clarification and, at the same time, suggests a new direction of investigation for the ultimate understanding of the glass transition phenomenology.

References

- [1] P. W. Anderson, expressing a viewpoint in the journal *Science*, **267**, 1616 (1995).
- [2] P.G. Debenedetti, *Metastable liquids*, Princeton University Press, NJ, (1996).
- [3] C.A. Angell, *Science*, **267**, 1924 (1995).

Principal Publication and Authors

T. Scopigno (a), G. Ruocco (a), F. Sette (b) and G. Monaco (b), *Science* **302**, 850 (2003).
 (a) INFM and Università di Roma “La Sapienza” (Italy)
 (b) ESRF