Fragile-to-Strong Transitions in Glass Forming Liquids.

Pierre Lucas

Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA

Abstract: Since they were first reported almost two decades ago, fragile-to-strong (FTS) transitions have been observed in all categories of glass-forming systems including metallic, covalent, ionic and molecular liquids. In these systems, a transition from Arrhenius to non-Arrhenius viscosity behavior is observed in conjunction with anomalies in multiple thermodynamic variables including the heat capacity, the thermal expansion coefficient and the isothermal compressibility. A review of experimental evidences supporting the existence of FTS transitions is presented. In particular FTS transitions are found to be concomitant with a peak in heat-capacity as well as density extrema associated with a negative expansion coefficient in the region of the transition. Moreover, spectroscopic analyses also show distinct structural changes across these liquid-liquid transitions. Reports of FTS transitions in each category of liquid are reviewed.

1. Introduction:

Glass parts of complex shapes are easily fabricated by simply reheating amorphous solids into the viscous regime. This enables a broad range of advanced fabrication methods such as molding, drawing, blowing or floating which require refined control of the viscosity. In that respect, the viscosity-temperature dependence is central to the glass manufacturing process so that different glass forming melts have historically been labeled “long” and “short” to describe how quickly their viscosity change with temperature. This empirical observation was later generalized and quantified by Angell using the fragility scale and applied to all types of glass forming liquids beyond the traditional industrial silicate systems [1, 2]. It was found that the viscous behavior of almost all glass formers can be conveniently compared on a universal plot of viscosity against temperature scaled by the glass transition temperature $T_g$. The first use of such plots is attributed to Laughlin and Uhlmann [3]. Angell later applied it to a broader range of glass-formers and introduced the concept of fragility where systems obeying a strict Arrhenius dependence of $\log \eta$ vs $T_g/T$ such as GeO$_2$ are labeled “strong” while systems showing a pronounced non-Arrhenius dependence such as toluene are labeled “fragile” as depicted in Fig. 1. A fragility parameter $m$ defined as the slope of the viscosity-temperature dependence at $T_g$ (equation 1) can then be used to classify glass-forming liquids spanning all temperature ranges.

$$m = \frac{d \log \eta}{dT_g/T} \bigg|_{T = T_g}$$

In most cases the temperature dependence of the viscosity can be accurately fitted with a model equation such as Vogel-Fulcher-Tammann (VFT) [4] or MYEGA [5] and the large majority of glass-formers can be fitted using a single fragility parameter $m$. 
As originally pointed out by Adam & Gibbs [6], the kinetics of glass forming liquids is directly related to thermodynamics through the configurational entropy $S_c$. Kauzmann [7] also long ago emphasized that certain liquids loose configurational entropy at a much faster rate than others upon cooling. This suggests that fragility may have a link to thermodynamics. Indeed, Martinez & Angell [8] have shown that the reduced configurational entropy $S_{exc}(T_g)/S_{exc}(T)$ constitute a thermodynamic signature of fragility that closely mimics the change in viscosity. This is illustrated in Fig. 2, where the reduced entropy patterns of the two archetypical strong and fragile liquids GeO$_2$ and toluene qualitatively reproduce the viscosity patterns represented in Fig. 1. This pattern is found for liquids spanning the whole range of fragility [8, 9]. A link between thermodynamic and kinetics of glass-forming liquids had also been made by Moynihan et al. [10] who showed that the activation energy for enthalpy relaxation closely match that for viscous flow, although a small divergence is found in highly fragile systems [11]. Hence, the fragility of glass-formers can be investigated and characterized through both dynamic and calorimetric methods [12, 13].

Fig. 1. Angell’s fragility plot. The archetypical strong liquid GeO$_2$ [2, 14, 15] and fragile liquid toluene [16] are compared with the anomalous behavior of water [17, 18] and Ge$_{15}$Te$_{85}$ [19]. The viscosity temperature dependence of water and Ge$_{15}$Te$_{85}$ diverges far above $T_g$ and cannot be describe using a conventional VTF or MYEGA equation. The lines for GeO$_2$ and toluene are guide to the eyes.
Fig. 2. Thermodynamic fragility plot represented by the reduced entropy versus inverse temperature normalized by $T_g$ [8]. The thermodynamic fragility is derived from calorimetric measurements for GeO$_2$, toluene, water and Ge$_{15}$Te$_{85}$ [9, 20]. Water and Ge$_{15}$Te$_{85}$ show a transition from fragile to strong consistent with the viscosity behavior. In comparison the standard liquids GeO$_2$ and toluene exhibit a conventional strong and fragile behavior respectively. The lines for GeO$_2$ and toluene are guide to the eyes.
2. Fragile-to-Strong Transitions

2.1. Viscosity anomaly

It was recognized early on that the viscosity of certain liquids such as BeF$_2$ did not fit the universal pattern of fragility [21]. However, the first report of a FTS transition was made for water by Ito et al. [22]. It was deduced from the mismatch between the highly fragile viscous flow at high temperature compared to the broad width of the $T_g$ which indicated a very strong liquid at low temperature. The existence of this FTS transition is consistent with an anomaly in the viscosity-temperature dependence of water as depicted in Fig. 1 [17, 18] and first pointed out by Speedy & Angell [23]. The viscosity temperature dependence of water diverges far below $T_g$ and cannot be fitted using conventional model equations. Unfortunately, viscosity measurements at lower temperature are precluded by crystallization so that the full FTS transition is masked and only the onset is revealed. A similar behavior is observed in the covalent melt Ge$_{15}$Te$_{85}$ [19] as recently pointed out in several studies [24, 25]. The viscosity shows a sharp divergence following a power law [24] that is not compatible with conventional models (Fig. 1).

2.2 Heat capacity anomaly

The transition in viscous behavior is also found to occur concomitantly with an anomaly in calorimetric measurements as depicted in Fig. 2&3. In particular, a pronounced overshoot of the liquid heat capacity is found in water [26] and Ge$_{15}$Te$_{85}$ [27] in the same temperature range as the viscosity divergence (Fig. 3). The heat capacity measurement for water is interrupted by crystallization but Starr et al. [9] extrapolated these values with low temperature calorimetric data to model the reduced entropy over the full temperature range. Their model predicted a thermodynamic fragility transition with a “double kink” as illustrated in Fig. 2. That pattern was recently supported by molecular dynamic simulations [28]. Interestingly the heat capacity data acquired by AC calorimetry for Ge$_{15}$Te$_{85}$ covers the full supercooled liquid regime and permit to obtain a continuous and complete measurement of the reduced entropy across the FTS transition (Fig. 2) [20]. The resulting curve confirms the “double kink” form of the thermodynamic fragility across the FTS transition. In addition, an Adam-Gibbs analysis of these data confirms that the viscosity follows the same pattern. The viscosity data derived from this analysis match the experimental values well and extend them to show the “double kink’ form [24].

3.2 Density anomaly

In addition to the viscosity and heat capacity anomalies, FTS transitions are commonly associated with an anomaly in density as depicted in Fig. 4 for Ge$_{15}$Te$_{85}$ [29] and water [30]. While the standard liquids GeO$_2$ and toluene show a conventional decrease in density with increasing temperature, water and Ge$_{15}$Te$_{85}$ instead exhibit a negative expansion coefficient in the region of the FTS transition. At high temperature, water and Ge$_{15}$Te$_{85}$ have a rate of density change similar to that of the fragile liquid toluene, however, in the range $T_g/T = 0.5$-.6 they exhibit a density maximum and a switch to a negative expansion followed by a density minimum.
and finally a switch to a rate of density change similar to that of the strong liquid GeO$_2$. Hence, the density also appears to exhibit a pattern consistent with a transition from a fragile to a strong behavior.

Fig. 3. Comparison of the anomaly in (a) viscosity $\eta$, (b) heat capacity $C_p$ and (c) thermal expansion coefficient $\alpha$ for water [31, 32] and Ge$_{15}$Te$_{85}$ [29]. The three quantities show a divergence in the same temperature range corresponding to the fragile-to-strong transition. The $C_p$ data for water [26] are interrupted by crystallization while the data for Ge$_{15}$Te$_{85}$ were collected through the entire supercooled region using AC calorimetry [27].
Fig. 4. Temperature dependence of the normalized density for glass forming liquids GeO$_2$ [33], toluene [34], Ge$_{15}$Te$_{85}$ [29] and water [30]. GeO$_2$ and toluene show a conventional decrease in density with increasing temperature while Ge$_{15}$Te$_{85}$ and water exhibit a negative expansion coefficient in the range of the fragile-to-strong transition. The dotted line is from ref. [35].

The hypothesis that these three anomalies are related to the same phenomenon is supported by the fact that they occur concomitantly in a relatively narrow range of temperature as depicted in Fig. 3. The heat capacity $C_p$ and thermal expansion coefficient $\alpha$ show a sharp maximum at the same temperature which is also concomitant with the overshoot in viscosity. In addition, Kanno et al. [36] pointed out that a sharp maximum in isothermal compressibility also occurs at the same temperature in water, and Tsuchiya [29] reported the same in Ge$_{15}$Te$_{85}$. Such sudden change in multiple physical properties is indicative of a liquid-liquid phase transition (although not necessarily first-order) associated with the switch from fragile to strong behavior.
3. Chalcogenide melts:

The type of transition described above for Ge$_{15}$Te$_{85}$ appears to be present in several other telluride melts. Although viscosity data is limited, heat capacity overshoots are systematically observed in Ge-Te, Ge-As-Te and some Ge-Sb-Te melts [27, 37]. Density anomalies are also found systematically in Ge-Te [29] but viscosity and density data are lacking for Ge-As-Te and Ge-Sb-Te. In addition, a FTS transition has been reported in Ag-In-Sb-Te based on viscosity estimates from crystal growth measurements [25]. Moreover, spectroscopic analysis of Ge$_{15}$Te$_{85}$ melts indicate some short-range and medium-range order structural changes across the FTS transition [20].

Besides telluride melts, FTS transitions are also observed in several selenide systems. A FTS transition was recently reported in GeSe$_2$ based on a combination of calorimetric and viscosity data [38]. But such transitions are broadly found across the Ge-Se system as described in Fig. 5&6. Viscosity data available over multiple ranges of temperature reveal a viscosity transition in Ge-Se melts containing significant fractions of Ge [39-42]. Data compiled for GeSe$_3$ are shown in Fig. 5 and compared with that for pure Se. While the viscosity of Se can be fitted with a single fragility parameter, the viscosity of GeSe$_3$ shows a distinct transition from a fragile behavior at high temperature to a stronger behavior at low temperature. The entire set of viscosity data cannot be fitted with a single fragility parameter $m$. Such transitions are also found in Ge$_{20}$Se$_{80}$ and Ge$_{30}$Se$_{70}$ [39-42]. High temperature viscosity data for chalcogenide melts were corroborated by different techniques including capillary and oscillation viscometry [43, 44]. Moreover the vapor pressure was monitored to insure that it would not affect the viscosity measurement [44]. The low temperature viscosity data were also corroborated by multiple techniques in independent studies [39, 40, 45]. This attests that FTS transitions such as that shown in Fig. 5 are not artefacts of measurement techniques but correspond to a genuine liquid-liquid transition. This is further substantiated by the presence of a density anomaly in the same temperature range as shown in Fig. 6. This behavior is analogous to that of water and Ge$_{15}$Te$_{85}$ (Fig. 4). The switch to a negative expansion coefficient is observed at the same temperature as the viscosity divergence for each composition. For Se, on the other hand, no anomaly is found in either the viscosity or density. An identical density anomaly concomitant with a viscosity divergence was also observed in several GeAsSe melts [46]. In this system, the effect is more pronounced with increasing Ge content as well. This could indicate that the tetrahedral nature of Ge may promote the development of FTS transitions. Unfortunately no heat-capacity data is available in this range of temperature to confirm the calorimetric signature of these FTS transitions.

As recently discussed by Wei et al. [37], fragile-to-strong transitions in chalcogenide systems are also associated with a semiconductor-to-metal transition. This type of liquid-liquid phase transitions may be critical for the operation of phase change materials [47].
Fig. 5. Viscosity-temperature dependence of GeSe$_3$ [39-42] exhibiting a fragile-to-strong transition. The viscosity data for GeSe$_3$ cannot be fitted with a single MYEGA or VTF equation in contrast to Se [43, 45] which is well fitted with a single fragility parameter over the full temperature range.
While Se shows a conventional decrease in density with increasing temperature, introduction of Ge generates an increasingly pronounced negative expansion coefficient. For each composition, the density anomaly occurs in the same temperature region as the viscosity divergence. The line for Se data is a guide to the eyes.

4. Halide melts:

The presence of FTS transitions has also been reported in halide melts such as BeF$_2$ [50] and ZnCl$_2$ [38]. Interestingly BeF$_2$, ZnCl$_2$ and GeSe$_2$ have the same short range order in the sense that they are all built from tetrahedral motifs. However they may have different medium range order. BeF$_2$ is formed of corner-sharing tetrahedra [51] while GeSe$_2$ contains large fractions of
edge-sharing tetrahedra [52]. In that respect, molecular dynamic simulations by Wilson & Salmon [53] indicated that the fragility of tetrahedral liquids increases with the number of edge-sharing motifs. This was consistent with the observation that systems dominated by corner sharing tetrahedra such as GeO₂ and SiO₂ are strong while systems with larger fractions of edge sharing tetrahedra such as GeSe₂ are more fragile. But the fraction of edge-sharing tetrahedra is also found to increases with temperature in melts such as ZnCl₂ [54] and Ge-Se [55]. Expanding on that line of thought, a recent temperature-dependent Raman study of ZnCl₂ reported a notable change in conversion rate between edge- and corner-sharing motifs in the region of the FTS transition (see Fig. 7) [38]. At low temperature, the ratio of corner-to-edge-sharing tetrahedra (CS/ES) changes only slowly while it changes more rapidly at high temperature (Fig. 7a). This structural feature can in fact be related to the fragility behavior because the CS/ES ratio correlates to the configurational entropy $S_c$ due to the fewer topological degrees of freedom $f$ in edge-sharing motifs [38, 56]. It is indeed the rate of change of the configurational entropy $S_c$ that determines the departure from Arrhenius behavior, i.e. the fragility according to the Adam-Gibbs equation (Fig. 7b inset). This is in turn consistent with the observation that a stable CS/ES ratio is associated with a more Arrhenius (strong) behavior near $T_g$ while a rapidly changing CS/ES is associated with a more non-Arrhenius (fragile) behavior at high temperature. This provides a possible structural interpretation for the FTS transition in this melt.

At this stage there is no spectroscopic evidence that a similar change in CS/ES ratio is associated with FTS transitions in GeSe₂ or BeF₂ melts. Nevertheless, it is known that the CS/ES ratio decreases with temperature in Ge-Se melts and a liquid-liquid transition involving a conversion from a corner-shared high-density structure to a partly edge-shared low-density structure was observed in GeSe₂ under pressure [57]. Therefore, a correlation appears to exist between CS/ES and density in these melts. The switch in rate of density change observed through the FTS transition (Fig. 4&6) would then be consistent with a change in CS/ES conversion rate. But more spectroscopic analyses are required to confirm this hypothesis.
Fig. 7. Temperature dependence of (a) the corner- to edge-sharing tetrahedra ratio and (b) viscosity for ZnCl₂ [38]. The ZnCl₂ melts exhibit a fragile-to-strong transition concomitant with a change in conversion rate between corner- and edge-sharing tetrahedra. The Adam-Gibbs equation (b inset) indicates that the configurational entropy $S_c$ determines the Arrhenius behavior of the viscosity. Topological considerations [56] further indicate that $S_c$ correlates to the number of structural degrees of freedom $f$ and the ratio of corner- to edge-sharing tetrahedral (a inset), thereby providing a link between structure and viscous behavior.
5. Metallic melts:

The first set of viscosity measurement collected across an entire FTS transition was reported by Way et al. [58] on ZrTiCuNiBe alloys in the liquid and supercooled liquid state. A hysteresis was observed between cooling and heating with the viscosity transition occurring near 1100 K on heating and near 900 K on cooling. The transition was later shown to be concomitant with a heat capacity maximum and a distinct change in XRD structure factor attributed to a weak first order liquid-liquid transition [59]. Viscosity transitions were also reported in various ZrCuNiAl(Nb,Ti) alloys, based on the mismatch between low and high temperature viscosity behaviors [60]. The low temperature viscosity measured by beam-bending showed a strong behavior while the high temperature viscosity measured by Couette concentric cylinder viscometry showed a fragile feature. The transition in ZrCuNiAlNb alloys was also associated with a heat capacity maximum and a change in XRD structure factor indicative of a liquid-liquid transition [61].

FTS transitions were also reported in a wide range of metallic alloy compositions using calorimetric estimates of $m$ near $T_g$ and oscillation viscometry data at high temperature [62]. A modified MYEGA equation was proposed to fit the viscosity across the FTS transition. Relaxation studies on these hyperquenched alloys showed a non-monotonous enthalpy release upon annealing [63]. This was interpreted as the consequence of glasses being trapped in competing phases across the FTS transition during hyperquenching. A transition in medium range order observed by XRD also supported that hypothesis [64]. Furthermore, a link between the emergence of beta relaxation and the extent of FTS transition was observed in these systems [65]. The surprisingly broad range of alloy compositions exhibiting FTS transitions suggests that it may be an intrinsic feature of metallic glass-formers [60, 62].

6. Oxide melts:

Experimental investigations of oxide melts are usually difficult due to their refractory nature. Temperatures far above 2000K are often required to study their structure and dynamics [66, 67]. Hence, viscosity data in the high temperature region of fragility curves are scarce and can limit direct observation of FTS transitions in these systems. In addition, the thermodynamic boundaries of potential liquid-liquid transitions may be located in a region of the P-T diagram that is not easily accessible at ambient pressure [68, 69]. For these reasons, investigations of FTS transitions in oxide systems often rely on computer simulations or high-pressure measurements [68-73].

In that respect molecular dynamic simulations indicate that the archetypical strong system SiO$_2$ actually undergoes a FTS transition far above experimentally accessible temperatures near 3300K [70]. This transition is associated with a change in the distribution of inherent structures in the potential energy landscape [71]. This is in turn associated with a heat capacity maximum and negative expansion coefficient as in the case of water [68, 71]. In principle, crossing the
liquid-liquid coexistence line in the P-T diagram can be achieved by either temperature or pressure increase [69]. Hence, these simulation results help rationalizing previously observed pressure-induced polyamorphic transitions measured spectroscopically at room temperature in SiO2 glass [72]. Similar pressure induced polyamorphism has also been observed in GeO2 [73].

Another approach for investigating liquid-liquid transitions in oxides is to quench the melt with the aim of trapping distinct glassy phases from coexisting liquids. This is possible if the liquid-liquid phase transition is of first order. This is the case of Y2O3-Al2O3 where glassy phases of different density and structure but identical compositions were observed over the range 22-32 mol% Y2O3 [74]. Glassy inclusions with different refractive index and vibrational spectra suggested that two distinct liquid phases coexist just above the glass transition temperature at ambient pressure. A contactless aerodynamic levitation furnace was subsequently used to investigate the liquid in the supercooled state by avoiding heterogeneous nucleation [66]. X-ray scattering measurements in 20Y2O3-80Al2O3 revealed a sharp and reversible structural change near 1800K that was attributed to a first order liquid-liquid phase transition. However, these results have later been the subject of controversy [75].

Recently, FTS transitions were also observed in the CaO-Al2O3 system [67]. The high-temperature liquids were investigated by contactless aerodynamic levitation. The viscosity was estimated from the damped decay of the levitated drop oscillation following an acoustic stimulation. The low-temperature liquid dynamic was estimated by calorimetry. FTS transitions were thus observed across the compositional range CaO-2Al2O3 to 5CaO-Al2O3. Mismatch in molar volume and configurational entropy were also observed between the high-temperature and low-temperature phases.

7. Elemental melts:

Liquid-liquid transitions have also been reported in several elemental melts including Si, Ge and P [76-82]. High-pressure analysis of amorphous Si by Raman spectroscopy revealed a reversible phase transition near 14 GPa [76]. A low density tetrahedral amorphous phase obtained by chemical route was found to reversibly convert into a high density metallic phase upon pressure increase. This amorphous solid transition was found to map onto a liquid-liquid transition in the supercooled regime. Molecular dynamic simulation also showed that the liquid-liquid transition in Si is thermodynamically of first order [77]. These observations were consistent with previous predictions of an FTS transition from diffusion coefficient estimates [78].

A similar pressure induced phase transformation was observed in Ge by X-ray absorption spectroscopy [79]. Amorphous Ge produced by evaporation showed a discontinuous change in short range order when compressed to 8 GPa at ambient temperature, but the process was not reversible upon decompression as in the case of Si. A polyamorphic transition was also reported during laser melt-quenching of Ge under pressure [80]. Laser-pulse melting near 8 GPa produced
a melt-quenched, high-density, metallic form of Ge which transformed to low-density tetrahedral Ge upon decompression.

Finally, a reversible liquid-liquid phase transition was observed in phosphorus above its melting point upon compression to 1 GPa [81]. The observation of coexistent phases with distinct structures confirmed the first order nature of the transition. The low-pressure phase was composed of P₄ molecules while the high-pressure phase had a polymeric liquid structure. X-ray radiography further showed that the high-density phase nucleates and grew into immiscible drops within the low-density phase [82]. The difference in droplet dynamics qualitatively suggested a difference in viscosity thereby supporting a FTS transition.

8. Conclusion:

Since their first report almost two decades ago, FTS transitions have been observed in all categories of material systems. The transition from Arrhenius to non-Arrhenius viscosity behavior is associated with anomalies in multiple thermodynamic variables including the heat capacity, the thermal expansion coefficient and isothermal compressibility. For most systems, anomalies in thermodynamic variables such as \( C_p \) and \( \alpha \) show a rapid but continuous change across the FTS transition. Such continuous change is not indicative of a true first-order transition where two distinct phases coexist. Nevertheless, the structural changes observed across the transition indicate a transformation between two distinct liquids. Except for phosphorous which exhibits an unambiguous first-order liquid-liquid transition above its melting point, the presence of liquid-liquid transitions usually occurs in the supercooled state below the crystal-liquid coexistence line [69]. This makes their observation particularly challenging because of the inherent thermodynamic competition against crystallization and kinetic competition against vitrification. Hence, some of these transition have been inferred from the glassy state i.e. the related polyamorphic transitions. Except for metals, the majority of FTS transitions are observed in liquids with tetrahedral character. This would suggest that the three-dimensional open tetrahedral network usually associated with strong liquids such as SiO₂ or BeF₂ may favor the occurrence of FTS transition. In fact it was suggested that all liquids exhibiting a strong behavior at low temperature may be the result of a FTS transition at high temperature [71]. Nevertheless, more experimental and computational investigations are still required to clarify the underlying origin of FTS transitions. It is a rapidly growing topic of investigation, and such transitions have now also even been observed in biological systems such as proteins and DNA [83, 84].

Acknowledgement

PL acknowledge financial support from NSF-DMR under grant#: 1832817
References