



Letter to the editor

An experimental critique on the existence of fragile-to-strong transition in glass-forming liquids

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ABSTRACT

A number of recent studies in the literature have reported the existence of unusual temperature dependence of the shear viscosity for a variety of glass-forming liquids that cannot be described with a single fragility index. Rather, these liquids display an apparent fragile-to-strong transition (FST) with lowering of temperature that was suggested to be indicative of a structural transition. In the present work we critique the accuracy of the high-temperature oscillation viscometry technique that was used almost exclusively for viscosity measurements of these liquids above their liquidus temperature. Viscosity measurements are carried out on binary Ge-Se chalcogenide liquids in their supercooled and stable states using conventional capillary and parallel-plate rheometry techniques and are compared with the oscillation viscometry data in the literature. Such comparisons conclusively demonstrate that the latter measurement technique often underestimates the viscosity by nearly an order of magnitude, especially at high temperatures. These results, when taken together, indicate that the observation of FST in glass-forming liquids is likely an artifact of the inaccuracy of the oscillation viscometry technique. Moreover, these results cast serious doubt on the reliability of the high-temperature oscillation viscometry data for metals and alloys that are prevalent in the literature.

1. Introduction

Viscosity is a key transport property that is at the heart of the processing of a wide variety of liquids, including metals, alloys, glasses and polymers. The remarkable increase in viscosity of glass-forming liquids by more than twelve orders of magnitude with decreasing temperature in the supercooled regime holds the clue for an atomistic understanding of the phenomenon of glass transition [1]. The temperature dependence of the shear viscosity η of glass-forming liquids displays behaviors ranging from approximately Arrhenius, with an activation energy that is nearly independent of temperature, to strongly non-Arrhenius, where the activation energy increases rapidly with decreasing temperature. The degree of departure from an Arrhenius behavior has been used by Angell to classify glass-forming liquids into “strong” vs. “fragile” via the use of the fragility index m which is defined as [2,3]:

$$m = \left. \frac{d \log_{10} \eta}{d \left(\frac{T_g}{T} \right)} \right|_{T=T_g} \quad (1)$$

where T_g and T are the glass transition temperature and the absolute

temperature, respectively. In most cases, the temperature dependence of the viscosity of a glass-forming liquid can be described reasonably well, over the entire range of supercooling, using the Vogel–Fulcher–Tammann (VFT) equation [1]:

$$\log_{10} \eta = A + \frac{B}{T - T_0} \quad (2)$$

where A , B and T_0 are material-dependent constants. In this case, the fragility index can be expressed in terms of the VFT parameters as:

$$m = \frac{\left(\frac{B}{T_g} \right)}{\left[1 - \left(\frac{T_0}{T_g} \right) \right]^2} \quad (3)$$

Since, at $T = T_g$ the viscosity of any glass-forming liquid typically reaches a value of $\eta \approx 10^{12} \text{ Pa} \cdot \text{s}$, the $\log_{10} \eta$ vs. $\frac{T_g}{T}$ behavior of a glass-forming liquid over the entire range of supercooling is expected to be characterized by a single value of m . In a recent study Zhang et al. reported experimental viscosity data on a variety of metallic glass-forming liquids that displayed a violation of this behavior [4]. As these liquids are prone to crystallization at intermediate temperatures, the

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viscosity data were obtained near T_g using either calorimetric or three-point beam bending techniques and near the liquidus temperature with an oscillating viscometer. It was shown that the temperature dependence of the shear viscosity of these liquids cannot be explained with a single fragility index [4]. Rather, these liquids are characterized by a low value of m i.e. behave as strong liquids at low temperatures near T_g , while their viscosity near liquidus is characteristic of that of a fragile liquid with high m . This apparent fragile-to-strong transition (FST) with lowering of temperature was ascribed to a polymorphic transformation of the structure of these liquids with temperature. It was hypothesized that such a transformation is accompanied by the destruction of the medium-range and even short-range structural order in these liquids with increasing temperature [4]. It is to be noted here that such transitions were predicted by molecular dynamics simulations to be prevalent in tetrahedral glasses-forming liquids such as H_2O and SiO_2 [5,6].

A recent study by Lucas et al. reported fragility measurements on two other tetrahedral glass-forming liquids namely, $ZnCl_2$ and $GeSe_2$ using differential scanning calorimetry [7]. It was shown that an FST scenario, similar to that mentioned above, needs to be invoked when near T_g fragility data for both systems are compared to the high-temperature viscosity data available in the literature [7]. Conjectures regarding the existence of such a transition have also been made previously in the literature for other Ge-Se liquids as well as phase change telluride liquids (e.g. Ag-In-Sb-Te, Ge-Te), based on similar comparisons between the DSC-based fragility and the high-temperature viscosity data [8,9]. The ratio F of the high- and low-temperature fragilities has been used as an indicator of the strength of this transition which typically ranges between $2 \leq F \leq 8$, with metallic liquids being characterized by some of the highest F values [4].

It is clear from Eq. (1) that fragility m is defined at $T = T_g$. However, for many of the glass-forming liquids that display the FST, viscosity measurements are often not feasible near T_g due to their instability against crystallization or their extreme hygroscopic nature. Under these circumstances, any comparison between the fragility derived from fitting high-temperature viscosity data over a limited viscosity range and that obtained from calorimetric methods near T_g , has its caveats. In the case of $ZnCl_2$, the high-temperature viscosity was fitted to an empirical equation under the inherent assumption of a viscosity of 10^{12} Pa·s at $T = T_g$. While this assumption is quite accurate for oxide liquids, in the case of chalcogenides and halides the high-frequency shear modulus G_∞ is lower than 10^{10} Pa, which, on the basis of the Maxwell relation: $\eta = \tau \times G_\infty$ would result in a viscosity significantly lower than 10^{12} Pa·s at T_g corresponding to a relaxation time τ of $\sim 10^2$ s. For example, in the case of supercooled $ZnCl_2$ liquid, previous Brillouin scattering measurements [10] indicated $G_\infty \sim 10^{9.5}$ Pa near T_g , which would result in a lower value of the high-temperature fragility m' (~ 50) compared to that reported by Lucas et al. ($m' = 59$). On the other hand, the low-temperature fragility m can be calculated for this liquid using the empirical relation [11]: $m = 40 \frac{\Delta C_p(T_g)}{\Delta S_m}$, where $\Delta C_p(T_g)$ is the jump in heat capacity across glass transition and ΔS_m is the entropy of melting of crystalline $ZnCl_2$. Previously reported results [11] on $\Delta C_p(T_g)$ and ΔS_m of $ZnCl_2$ indicate $m \sim 40$ near T_g , compared to the value of $m \sim 30$ reported by Lucas et al. [7]. These estimates bring the high- and low-temperature fragilities quite close (50 vs. 40) and cast reasonable doubt on the existence of a fragile-to-strong crossover for $ZnCl_2$. However, similar corrections for the fragility values are not significant enough to question the validity of such a transition in the case of metallic or some chalcogenide liquids where the F ratios are significantly higher than that reported for $ZnCl_2$ [4,7–9]. It is important to note that compared to $ZnCl_2$, these latter classes of liquids are characterized by significantly higher melting points and the reported high temperature viscosities are measured exclusively using an oscillating viscometer.

Recent reviews of the viscosity measurement techniques that are commonly adopted at high temperature, especially for molten metals

and alloys, can be found in the literature [12–14]. Here we focus on the most commonly adopted technique of oscillation viscometry, since all reports in the literature on the fragile-to-strong transition in glass-forming chalcogenide and metallic liquids have exclusively used the high-temperature viscosity data generated by this technique. In the application of the oscillation technique the liquid under consideration is typically contained in a cylindrical vessel which is vertically suspended using a torsion wire and is set into oscillatory motion about the vertical axis. This motion is damped by the presence of the liquid due to its absorption and dissipation of the frictional energy and the viscosity of the liquid is determined from its relation to the time period of the oscillatory motion and its decrement which can be measured with relative ease. Relatively small amounts of liquid can be used with this technique, which allows for the attainment of stable thermal equilibrium and extremely low viscosities (1 mPa·s or less) can be measured [12–14]. In spite of the ease with which the technique can be used at very high temperatures under controlled atmosphere conditions and the parameters of the oscillatory motion can be measured, this method suffers from some serious disadvantages [12–14]. Most important among these is the fact that the viscosity is derived from the measured parameters through the solution of a second order differential equation of oscillatory motion of the system which also involves the approximate (linearized) solutions of the Navier-Stokes equations for the motion of the liquid in the container. In the case of a liquid in a cylindrical container the equation of motion for its damped oscillatory motion is [12,14]:

$$I \left(\frac{d^2\varphi}{dt^2} \right) + J \left(\frac{d\varphi}{dt} \right) + D(\varphi) = 0 \quad (4)$$

where I is the moment of inertia of the empty cup and suspension, t is time, D is the force constant of the torsion wire, φ is the angular displacement of any segment of the liquid from its equilibrium position and J is a function of the density ρ and the viscosity η of the liquid, the internal radius of the cylindrical container R and the height of the liquid H . There are several mathematical treatments for the solution of Eq. (4) that yield different viscosity values from the same experimental parameters. The most popular approach for determining the viscosity, which has been used in practically all studies on metallic and chalcogenide glass-forming liquids, is the analysis by Roscoe which relates viscosity to the period of oscillation θ , its logarithmic decrement between consecutive swings λ , H , ρ and R . According to the Roscoe approach, viscosity is expressed as [12,14]:

$$\eta = \left(\frac{I\theta}{\pi R^3 H Z} \right)^2 \frac{1}{\pi \rho \theta} \quad (5)$$

where, $Z = \left(1 + \frac{R}{4H} \right) a_0 - \left(\frac{3}{2} + \frac{4R}{\pi H} \right) \frac{1}{p} + \left(\frac{3}{8} + \frac{9R}{4H} \right) \frac{a_2}{2p^2}$; $p = \sqrt{\frac{\pi \rho}{\eta}} R$;
 $a_0 = 1 - \frac{3\lambda}{4\pi} - \frac{3}{8} \left(\frac{\lambda}{2\pi} \right)^2$; and $a_2 = 1 + \frac{\lambda}{4\pi} + \frac{1}{8} \left(\frac{\lambda}{2\pi} \right)^2$.

A major source of error in obtaining the viscosity from these experiments can be associated with the increasing experimental uncertainty in extrapolating H and R values at high temperatures [12–14]. Furthermore, previous studies have indicated that the wetting properties of the liquid are also important. For example, if the liquid does not wet the walls of the container then it may slip during the oscillation, which would result in increased damping. The wetting behavior may also be sensitively dependent on temperature and on any chemical reaction that may occur between the liquid and the container, especially at high temperatures [12–14]. Finally, it has been suggested that the effect of the liquid meniscus on H and the finite length of the cylindrical container have not been adequately weighted in the Roscoe treatment. Besides these inherent drawbacks of the technique, Cheng et al. [14] have recently noted that, unlike other viscosity measurement techniques, there are no specified standards that have been adopted for the oscillation viscometry technique. Thus, it is not surprising that, even as recently as in 1988, Iida and Guthrie [15] noted a spread of $\sim 400\%$ in

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