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Reconciling calorimetric and kinetic fragilities of glass-forming liquids

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ABSTRACT

The liquid fragility index (m_{vis}) describes the rate of viscosity change of a glass-forming liquid with temperature at the glass transition temperature (T_g), which is very important for understanding liquid dynamics and the glass transition itself. Fragility can be directly determined using viscosity measurements. However, due to various technical complications with determining viscosity, alternative methods to obtain fragility are needed. One simple method is based on measurement of the calorimetric fragility index (m_{DSC}), i.e., the changing rate of fictive temperature (T_f) with heating (cooling) rate in a small T_f range around T_g . The crucial question is how m_{DSC} is quantitatively related to m_{vis} . Here, we establish this relation by performing both dynamic and calorimetric measurements on some selected glass compositions covering a wide range of liquid fragilities. The results show that m_{DSC} deviates systematically from m_{vis} . The deviation is attributed to the Arrhenian approximation of the $\log(1/q_c) \sim T_g/T_f$ relationship in the glass transition range. We have developed an empirical model to quantify the deviation, by which m_{vis} can be well predicted from m_{DSC} across a large range of fragilities. Combined with the high- T viscosity limit ($10^{-2.93}$ Pa·s), we are able to obtain the entire viscosity curve of a glass-forming liquid by only performing DSC measurements.

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1. Introduction

The shear viscosity of glass-forming liquids is of great importance in all stages of industrial glass production [1–3]. Since viscosity is very sensitive to temperature and composition, we need to have accurate knowledge of the scaling of viscosity with both of these parameters. Viscosity is also critical for understanding the glass transition and the relaxation characteristics of liquids and their corresponding glasses. In the well-known Angell plot [4,5], the logarithm of viscosity, $\log_{10} \eta$, is plotted as a function of the T_g -scaled inverse temperature, T_g/T , where T is absolute temperature. With this scaling, Angell was able to compare the viscous flow behavior of all glass-forming liquids in a single universal plot. According to the Angell plot, there are three important parameters [6]: (i) the glass transition temperature, $T_g(x)$; (ii) the fragility, $m(x)$; and (iii) the extrapolated infinite temperature viscosity, $\eta_{\infty}(x)$. For any composition x , the glass transition temperature is defined as the temperature at which the shear viscosity is equal to 10^{12} Pa·s [7],

i.e., $\eta(T_g(x), x) = 10^{12}$ Pa·s. Fragility [8] is defined as the slope of the $\log \eta$ versus T_g/T at T_g :

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

The fragility index describes the rate of change in the liquid dynamics upon cooling through the glass transition. Liquids can be classified as either “strong” or “fragile” depending on whether they exhibit an Arrhenius or super-Arrhenius scaling of viscosity with temperature, respectively. While the fragility index itself is a first-derivative property of the viscosity curve, the degree of non-Arrhenius scaling reflects the second derivative of the viscosity curve with respect to inverse temperature. Following Angell [4,8], this non-Arrhenius scaling of liquid viscosity can be quantified directly through the fragility index (m_{vis} in this work) with the assumption of a universal high temperature limit of viscosity, i.e., $\eta_{\infty}(x) = \eta_{\infty}$. In our previous work [9], we have analyzed the viscosity data of 946 silicate liquids and other 31 non-silicate liquids; the results imply that the silicate liquids have a universal high temperature viscosity limit of around $10^{-2.93}$ Pa·s. Thus, we have validated Angell's assumption, which enables this direct connection between first- and second-derivative properties.

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Given the great importance of the fragility parameter, it has been the subject of extensive interest in both experimental and theoretical studies for many years [10–15]. While fragility is a kinetic property, it is closely correlated with various thermodynamic quantities of glass-forming liquids. For example, the change in heat capacity at the glass transition, width of the glass transition range, and configurational entropy loss at the glass transition all exhibit linear correlations with kinetic fragility [16–23]. An accurate determination of fragility is thus of great significance for understanding liquid physics near glass transition and for understanding the glass transition itself. Following the definition of fragility in Eq. (1), it should be directly determined using viscosity measurements. However, viscosity measurements are difficult for glass-forming systems, especially those systems with strong crystallization tendency and high liquidus temperatures. Liquid viscosity varies by over twelve orders of magnitude and requires specialized equipment in different viscosity and temperature regimes. Crystallization and volatilization of the melts can hinder high temperature viscosity measurements, while the specific sample size/shape demands and long measurement time impede the low temperature viscosity experiments. Therefore, alternative methods are needed to give an indirect quantification of fragility.

Various methods have been proposed to calculate fragility using differential scanning calorimetry (DSC). Moynihan and his co-workers found that the activation energy for structural relaxation determined by DSC is an accurate estimate of the activation energy for shear viscosity [24–27]. The activation energy for structural relaxation in the glass transition region can be determined from the cooling rate (q_c) dependence of the fictive temperature T_f measured using DSC.

$$\frac{d \ln q_c}{d(1/T_f)} = -\frac{E_g}{R}. \quad (2)$$

where E_g is the activation energy for equilibrium viscous flow in the glass transition region and R is the ideal gas constant. The fictive temperature, T_f , is defined here as the temperature at which the configurational enthalpy of the glass equals that of the corresponding liquid state [28]. This is obtained by an enthalpy-matching integral method using the heat capacity (C_p) curve during reheating [29]. It is found that when the prior cooling (q_c) and reheating rates (q_h) are the same, the T_f obtained using the integration method from the C_p reheating curve is very close to the onset glass transition temperature, $T_{g,onset}$ [24–26, 30]. For all the DSC measurements performed in this work, the reheating rates are equal to the preceding cooling rates. Therefore the $T_{g,onset}$ has been used as the fictive temperature T_f for the studied glasses in this paper.

Kissinger derived another equation to calculate activation energy for glass transition using DSC analysis at different scan rates [31]:

$$\ln \left(\frac{q}{T_f^2} \right) = -\frac{E_g}{RT_f} + \text{constant}. \quad (3)$$

After obtaining the activation energy E_g , the calorimetric fragility could then be calculated from E_g and T_g as

$$m = \frac{E_g}{2.303RT_g}. \quad (4)$$

Wang et al. [22,32] have deduced another equation to calculate calorimetric fragility in a more straightforward way:

$$\log \left(\frac{Q}{Q_s} \right) = m - m \frac{T_f^*}{T_f}. \quad (5)$$

Q is the DSC scan rate, Q_s and T_f^* correspond to a standard scan rate, and a standard fictive temperature T_f . The fictive temperatures for runs of different cooling rates are assessed by an enthalpy differencing procedure.

This is done by quantifying the enthalpy difference between the reheating scan of the glass previously cooled at the standard rate and the reheating scans of glass samples having different cooling rates. By incorporating Eq. (4) into Eq. (2), fragility can be obtained directly from the slope of the reduced cooling rate versus reciprocal reduced fictive temperature (or simply from the intercept) [22]. This is a modification of Moynihan's fictive temperature method, but the advantage is that the activation energy does not need to be obtained first to calculate fragility.

Yue et al. have investigated the physical correlation between the cooling rate dependence of the calorimetric fictive temperature and the temperature dependence of the equilibrium liquid viscosity [30,33,34]. The difference between both dependences is described by the equation $\log(q_c) = 11.35 - \log\eta(T_f)$. This means that both dependences differ by a shifting factor of 11.35, but their slopes at T_g are the same. The above equation indicates that the dependence of the cooling rate on the fictive temperature can be well described using a suitable viscosity model. Over a rather small range of the cooling rates, e.g., between 2 and 40 K/min, the slope of $\log(1/q_c) \sim T_g/T_f$ near T_g can be approximated as the calorimetric fragility (m_{DSC}). We have compared the fragility indices calculated by the several abovementioned methods, which produce generally the same values with the error range of ~ 1 . Actually Moynihan, Wang, and Yue's methods yield exactly the same value of fragility since they are all derived based on Arrhenian approximation, although they appear differently in equation form. Only Kissinger's equation gives a slightly different value, but the difference is no > 1 . In this work, we use the slope of $\log(1/q_c) \sim T_g/T_f$ near T_g as the m_{DSC} since it is the most direct and simplest method without calculating activation energy first.

Each of these calorimetric methods for determining fragility has an inherent assumption that the correlation of $\log(1/q_c) \sim 1/T_f$ is based on Arrhenius behavior near T_g . However, the actual scaling is non-Arrhenius across the whole temperature range. Therefore the Arrhenian approximation in the calculation may lead to the deviation between calorimetric fragility and kinetic fragility. There have been a few studies attempting to compare the two kinds of fragilities, and some deviation is found in organic and metallic glass-forming liquids [22,23]. However, a comprehensive evaluation of the deviation between kinetic fragility and calorimetric fragility for oxide glasses is not yet available.

In this paper, we have determined and collected both the kinetic and calorimetric fragility values of 20 borosilicate glasses, 6 soda-lime borate glasses, two fiber glass compositions (Rockwool (RW) and glass wool (GW) compositions), and 6 vanadium tellurite glasses (Table 1). The kinetic fragility (m_{vis}) is obtained by fitting the measured viscosity data to the Mauro-Yue-Ellison-Gupta-Allan (MYEGA) equation [6]. The m_{DSC} is determined as the slope of $\log(1/q_c) \sim T_g/T_f$ [30,33]. The calorimetric fragility of the studied glasses is compared with the kinetic fragility. If the quantitative link between kinetic and calorimetric fragilities is established, the viscosity of glass forming liquids could be determined solely by performing DSC measurements. Since viscosity measurements can be very challenging for some glass compositions, it is useful to supply an alternative way to determine viscosity.

2. Experimental procedure

All glasses were prepared by using the melt-quenching method. The details of sample preparation can be found in [35–41]. In order to determine the liquid fragility index, viscosity measurements were performed. The low viscosities (approximately $10^0 - 10^3$ Pa·s) were measured using a concentric cylinder viscometer, while the high viscosities (approximately $10^{10} - 10^{13}$ Pa·s) were determined by micro-penetration viscometry. For some of the compositions, we also performed beam bending and parallel plate compressing experiments. More information on the viscosity measurements is supplied in [36,38, 40]. The measured viscosity data are fitted to the MYEGA model to obtain $T_{g,vis}$ and m_{vis} [6].

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