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Phase change alloy viscosities down to $T_g$ using Adam-Gibbs-equation fittings to excess entropy data: A fragile-to-strong transition

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A striking anomaly in the viscosity of Te$_{85}$Ge$_{15}$ alloys noted by Greer and coworkers from the work of Neumann et al. is reminiscent of the equally striking comparison of liquid tellurium and water anomalies documented long ago by Kanno et al. In view of the power laws that are used to fit the data on water, we analyze the data on Te$_{85}$Ge$_{15}$ using the Speedy-Angell power-law form, and find a good account with a singularity $T_s$ only 25 K below the eutectic temperature. However, the heat capacity data in this case are not diverging, but instead exhibit a sharp maximum like that observed in fast cooling in the Molinero-Moore model of water. Applying the Adam-Gibbs viscosity equation to these calorimetric data, we find that there must be a fragile-to-strong liquid transition at the heat capacity peak temperature, and then predict the "strong" liquid course of the viscosity down to $T_g$ at 406 K (403.6 K at 20 K min$^{-1}$ in this study). Since crystallization can be avoided by moderately fast cooling in this case, we can check the validity of the extrapolation by making a direct measurement of fragility at $T_g$, using differential scanning calorimetric techniques, and then comparing with the value from the extrapolated viscosity at $T_g$. The agreement is encouraging, and prompts discussion of relations between water and phase change alloy anomalies.

I. INTRODUCTION

Upon undercooling, glass-forming liquids become increasingly viscous and, if crystallization is avoided, they eventually fall out of equilibrium and vitrify at their glass transition temperatures $T_g$. On approaching $T_g$, some liquids exhibit a near-Arrhenius rise in viscosity while others show a range of non-Arrhenius to highly non-Arrhenius behavior—the former of these are classified as "strong" liquids and the latter as "fragile" liquids according to the fragility concept. Frailty is commonly characterized by measuring the slope of the $T_g$-scaled Arrhenius-plot (fragility-plot)$^1$ at $T_g$, called "steepness index" or "m-fragility," $m = \frac{\partial \ln \eta}{\partial (T_g - T)} |_{T=T_g}$. A phenomenon called fragile-to-strong transition has attracted both interest and confusion, and is the subject of this paper. At its clearest, the term refers to a drastic change in the temperature dependence of viscosity from a high-temperature fragile liquid to a low-temperature strong liquid near $T_g$. Such a transition has been initially identified in water$^4$ and then suggested for other liquids.$^5$ On identifying a fragile or strong behavior of a liquid, there is a frequent confusion in characterizing "strong" behavior. A strong liquid should not be confused with a mere Arrhenius fit over a limited temperature range regardless of pre-exponent value, but is ideally the behavior that combines Arrhenius behavior with a pre-exponent near the phonon cycle time ($10^{-14}$ s) (or correspondingly viscosity $10^{-3}$ Pa s (Ref. 1), or diffusivity $10^{-7}$ m$^2$ s$^{-1}$).

The case of water is complicated by crystallization.$^1$ Starr et al.$^4$ used the assumption of heat capacity ($C_p$) continuity across the “no-man’s land,” and the Adam-Gibbs equation$^2$ to argue that a “double kink” in viscosity is what should characterize an unambiguous fragile to strong transition. Such a case has recently been seen in a model of silica with a large $C_p$ spike, but cut short by lack of computer simulation time. As a related system, silicon$^5$ has an increasing $C_p$ as it is cooled below $T_m$ similar to that observed in water.$^1$ With further undercooling performed in computer simulations, $C_p$ drops sharply at a first order transition$^3$ to exhibit a strong liquid value,$^2$ although high-temperature liquid silicon is fragile. Evidence for strong-fragile transitions has also been provided for a wide variety of bulk metallic glass-forming liquids, characterized by remarkable difference in strength parameter $D$ values obtained from viscosity data fits using the Vogel-Fulcher-Tammann (VFT) equation,$^9$ in the respective high and low temperature domains on either side of the crystallization gap. These have been supported by studies of structural changes in the liquid.$^{14,15}$ Simulations$^{16,17}$ showed that even a simple attractive Jagla potential can produce fragile-to-strong transition behavior, implying such a phenomenology may exist in a variety of materials, particularly model materials like the “patchy” colloids described by Sciotino and coauthors.$^{18,19}$

Here, we identify an unusually clear example in the behavior of some chalcogenide alloys with especially sharp but continuous heat capacity anomalies. The striking similarity of elemental Te to water was demonstrated some time ago by Kanno et al.$^{20}$ Both liquid Te and water show a pronounced $C_p$ anomaly and density maximum.$^{20}$ Tsuchiya and co-workers$^{21}$ have found that the alloy Te$_{85}$Ge$_{15}$ has an even sharper $C_p$ anomaly, which, unlike water, can be followed through a maximum down to $T_g$ so that the complete

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anomaly can be observed. A corresponding sharp anomaly in the viscosity was identified by Neumann et al. and noted by Orava et al. in a recent article concerned with the connection between fragility and phase-change random-access memory behavior. Finding the idea of a possible link between the two phenomenologies attractive, we have analyzed and applied the Adam-Gibbs equation to the heat capacity and viscosity data to produce an extrapolation to the glass transition domain, where the validity of the extrapolation can be checked by direct fragility measurements using differential scanning calorimetry (DSC). The course of the viscosity predicted by our procedure clearly shows the existence of the “double kink” form previously only “seen” by thermodynamic arguments for the viscosity of water and recently “observed,” by molecular dynamics simulation, in the diffusivity of a primitive model of silica. While it is less distinct than that for the case of water, a reflection of a weaker transition, it has the advantage of being based on actual, rather than derived, thermodynamic data. Accordingly, it adds plausibility to the arguments for the viscosity of water phenomenology being a liquid state rather than a pre-crystallization phenomenon. The reality of a continuous fragile-strong transition in the present case is important because, in the water case and also the metallic glass-former cases, the possibility of first order character in the transition cannot be excluded, indeed is even the more probable scenario according to some arguments.

Conversely, the possible occurrence of water-like fragile-to-strong transitions during hyperquenching (as in the sputtering process) could help in the understanding of important aspects of successful phase change memory behavior, as an insightful reviewer has pointed out (and as one of us originally speculated). We take this up in our Sec. IV.

II. MATERIALS AND METHODS

Amorphous $T_{g}$-samples were prepared by melting Ge and Te elements with purities ranging from 99.999 to 99.999 at. % under vacuum in a silica tube. After introducing the elements into the silica tube, the tube was sealed under vacuum and annealed in a rocking furnace for homogenization at $800 \,^\circ \text{C}$ for 8 h. The melt was then quenched into ice water to obtain amorphous $T_{g}$-samples. Calorimetric measurements were performed with a Q1000 MDSC from TA Instruments. Amorphous $T_{g}$-samples with mass from about 5–15 mg were sealed in aluminum pans and an empty aluminum pan was used as a reference. DSC cell calibration was carried out with standard sapphire. Temperature and enthalpy calibrations were performed for each heating rate with standard indium prior to measurements.

For fragility determinations using the DSC, we use both the Wang-Velikov-Angell (WVA) method and a modification of it that has advantages over the original “area matching method” for the samples of this study. While the Moynihan area matching method (Fig. 1(b)) for determining the fictive temperatures used in the WVA method had the advantage of avoiding dependence on the instrument behavior in the glass transformation zone, it requires an exceptionally stable instrument baseline for the curves to all meet at the higher temperatures. In our modification, we define the fictive temperature $T_f$ from the onset glass transition temperature $T_f^{onset}$ (Fig. 1(a)) for the case where cooling and heating scans are made at the same rate (shown true by Fig. 2 of Ref. 28), and then proceed with the analysis as in WVA. Note that $T_f\approx T_f^{onset}$ holds only if the same cooling and heating rates are used; otherwise (e.g., fixing a cooling rate), $T_f^{onset}$ is not an appropriate quantity for determining fragility.

In detail, to obtain a fragility value, each amorphous sample, in its sealed pan, was heated in the DSC to 180 $^\circ \text{C}$ (i.e., well above $T_g$ into the supercooled liquid), then cooled down to well below $T_g$ (to 25 $^\circ \text{C}$) at a selected cooling rate, after which an up-scan through $T_g$ at the same rate was performed immediately. In this scan, the heating was continued to 300 $^\circ \text{C}$ or until crystallization of the sample occurred. Then, the crystallized sample was cooled and re-scanned up to 300 $^\circ \text{C}$ at the same rate (“crystal state run”), serving as the baseline of the “amorphous run.” The same procedure was performed with different cooling and heating rates of 3, 6, 10, 20, 30 K min$^{-1}$ (see Fig. 1(a)). In so doing, the onset temperatures of the glass transition were determined using the baseline-subtracted up-scans for a given cooling and heating rate.

Despite the different way of obtaining $T_f$, we can still make use of the plot of the logarithm of scaled rate $\log q/q'$ versus scaled fictive temperature $T_f/T_f'$, used by Wang et al., to determine the temperature dependence of relaxation times across the standard $T_g$ (i.e., the fragility). In such a plot, $q$ is the cooling (=heating) rate and $T_f$ is the fictive

![FIG. 1. (a) Excess heat capacity measured upon heating at $q_h$ after previous cooling from 180 $^\circ \text{C}$ at the same rate $q_c=q_h$. The onset temperature of the glass transition is determined by tangent lines construction. (b) The “area matching” method for determining the fictive temperature $T_f$. The up-scans were performed at a constant heating rate 20 K min$^{-1}$ after various cooling rates, 3, 6, 10, 20 and 30 K min$^{-1}$. The curves are vertical shifted to align at 100 $^\circ \text{C}$.](image-url)
temperature corresponding to this \( q \). The scaling parameter \( q_s \) is the standard rate 20 K min\(^{-1} \) and \( T_f \) is the standard fictive temperature corresponding to \( T_f \) measured at the standard rate \( q_s = 20 \) K min\(^{-1} \). As derived in Ref. 26, both the best fit slope and the intercept then conveniently yield the \( m \) fragility value\(^{26} \) without further calculation (see Sec. III).

Knowledge of the fragility near \( T_g \) provides a key part of the argument for successful use of the Adam-Gibbs equation in establishing the presence of a fragile-to-strong transition in a liquid of marginal glass-forming ability, like liquid Te\(_{85}\)Ge\(_{15}\), as we show in Sec. IV.

III. RESULTS

As illustrated in Fig. 2(a), Te\(_{85}\)Ge\(_{15}\) is a eutectic composition with a low melting point. Figure 2(b) shows the heat flow measured during heating and during cooling at 10 K min\(^{-1} \) from room temperature to 500 °C using DSC. With increasing temperature, the amorphous sample of Te\(_{85}\)Ge\(_{15}\) undergoes a glass transition at about 130 °C, followed by crystallization at 214 °C, and finally sharp eutectic melting \( T_c = 385 °C \) = 658 K. From the melting peak, the enthalpy of fusion is determined \( \Delta H_m \approx 10.03 \) kJ mol\(^{-1} \) (estimated error 0.5%). Thus, the entropy of fusion is estimated by \( \Delta S_m = \Delta H_m / T_c \approx 15.24 \) J mol\(^{-1} \) K\(^{-1} \) (error 0.5%).

Figure 3 shows the data obtained by the procedures described in Sec. II for Te\(_{85}\)Ge\(_{15}\). A linear fit yields a fragility value of \( m = 49 \pm 4 \) for \( T_g \) determined from the equal scanning rate \( (q_h = q_c) \) as shown in Fig. 1(a), while the area-matching method (Fig. 1(b)) results in \( m = 54.5 \pm 3 \). This directly measured value indicates that Te\(_{85}\)Ge\(_{15}\) is an intermediate liquid near \( T_g \). The same results are obtained by determining the activation energy \( E_a \) at \( T_g \) from the conventional used plot of \( \ln(q) \) vs \( 1/T \) (here \( T_g \)) and taking the slope, \( E_a / R \) (see Fig. 3(b)). \( E_a \) is related to fragility by \( m = E_a / (\ln(10) T_g R) \), where \( T_g = 403.6 \) K is the glass transition temperature measured at 20 K min\(^{-1} \) following the same rate cooling (i.e., relaxation time \( \tau \approx 100 \) s), and \( E_a / R \) is the negative slope of the plot \( \ln(q) \) vs. \( 1/T \) (Ref. 27).

We now show, using the Adam-Gibbs equation, how this result can be used to “lock in” the identification of a fragile-to-strong transition in liquid Te\(_{85}\)Ge\(_{15}\) and what this might imply both about the nature of water, on the one hand, and important aspects of the phase change alloy phenomenology, on the other.

Before leaving this section, however, it should be noted that a previous study\(^{27} \), using DSC scans, reported a very
different value \( m = 120 \) for \( \text{Te}_{85}\text{Ge}_{15} \), much higher even than suggested for \( \text{Ge}_{3}\text{Sb}_{2}\text{Te}_{5} \). While the reason for the major discrepancy is not fully understood, we note that the protocol used in Ref. 31 study was not one of those recommended. During the initial heating, their samples were not taken far enough above \( T_g \) (10 degree higher than \( T_g \)) to establish a (metastable) thermodynamic equilibrium in the supercooled liquid before subsequent down- and up-scans. The compounding of thermal history effects in such a protocol deserves systematic study. A recent DSC study \(^{32} \) of \( \text{GeTe}_4 \) reported values of activation energy near \( T_g \), from which fragility can be derived, \( m \approx 48 \) (TNM model fitting) and \( m \approx 64 \) (area-matching method). Although the composition is slightly different, the values are consistent with our result.

IV. DISCUSSION

A. Viscosity and fragility

Liquid fragility is believed to play an important role in the glass-forming propensity of metallic glass-formers, and its recent connection to the phenomenology of chalcogenide-based phase-change materials used for data storage applications \(^{33-35} \) was highlighted in the introduction to this paper. Figure 4(a) is a \( T_g \)-scaled Arrhenius plot \(^1 \) used to compare the viscosity behavior of various chalcogenide glass-forming liquids. It includes, as a dashed line based on the crystallization rate study, the viscosity behavior of the ternary composition \( \text{Ge}_{3}\text{Sb}_{2}\text{Te}_{5} \) that is used for optical data storage and is regarded as the base composition for non-volatile electronic memory devices. \(^{33,36} \) The related binary system \( \text{Te}_{85}\text{Ge}_{15} \) shows a striking anomaly in the viscosity as it approaches its eutectic melting point \( T_e \). Such an anomalous rise by one order of magnitude in viscosity resembles the viscosity anomaly of supercooled water just before its crystallization (see Fig. 4(b)). \( \text{Te}_{85}\text{Ge}_{15} \) is a Te-based semi-metallic alloy; liquid Te and water show analogous heat capacity and density anomalies, as shown in the inset of Fig. 4(b). \(^{20} \) It is therefore interesting to hypothesize that \( \text{Te}_{85}\text{Ge}_{15} \) possesses a water-like fragile-to-strong transition near its eutectic point \( T_e \) that is not hidden by crystallization. We now develop an argument, using the Adam-Gibbs equation and available heat capacity data on this composition, to test this hypothesis.

In the light of the power laws that are used to fit the data on water, we first analyze the viscosity data of \( \text{Te}_{85}\text{Ge}_{15} \) using the Speedy-Angell power-law form \(^{15,46} \)

\[
\eta = A_\eta \left( \frac{T - T_e}{T_s} \right)^{-\gamma_\eta},
\]

where \( \eta \) is viscosity, \( A_\eta \) and \( \gamma_\eta \) are constants, and \( T_e \) being a singular temperature. As shown in the simple linear plot, Fig. 5(a), the viscosity rises sharply as \( T_e = 658 \) K is approached. The line through the points shows that Eq. (1) gives a good account of the data, yielding a constant \( A_\eta = 2.61 \times 10^{-4} \) Pa s, an exponent \( \gamma_\eta = 1.42 \pm 0.09 \), and a singular temperature \( T_e = 633 \pm 1 \) K, which is only 48 K below the peak of the heat capacity anomaly, (and 25 K below the eutectic temperature \( T_e \)). Figure 5(b) shows the viscosity with the same fitting line in the fragility-plot, clearly belonging to the fragile liquid class of behavior. If the anomalous rise near \( T_e \) is disregarded, the high-temperature fragility appears to be similar to that of \( \text{Ge}_{3}\text{Sb}_{2}\text{Te}_{5} \) estimated by Orava \textit{et al.} \(^{23} \), for which \( m \approx 90 \).

B. Heat capacity anomaly

As already mentioned, the \( \text{Te}_{85}\text{Ge}_{15} \) liquid also has an accompanying heat capacity anomaly which is distinguished from the water case by exhibiting a sharp maximum (see
Fig. 6). The maximum occurs in the stable liquid domain and can be followed well down into the supercooled liquid range, before crystallization preempts further measurements (Fig. 2(b)) and even to \( T_g \) (Fig. 7(a)). (In other words, this system has no "no-man’s land."

It is interesting to report that, where the anomaly in the case of water can be fitted by Eq. (1) using a singular temperature that is the same as that fitting the viscosity (and all other relaxation functions), the heat capacity data of Te\(_{65}\)Ge\(_{15}\) can only be fitted by this equation above the peak, and the fitting produces large errors in the values of the parameters. Like the fast cooling equation above the peak, and the fitting produces large errors for this phenomenon, even though a reliable method of estimating the non-anomalous "background" contribution to the total heat capacity is available.

C. Entropy, the Adam-Gibbs prediction of viscosity and fragility, and validation by DSC fragility values at \( T_g \)

In order to link the two phenomenologies, viscosity, and heat capacity, we apply the Adam-Gibbs equation\(^{12}\) which links viscosity to the configurational entropy content of the liquid and explains the deviation of the viscosity from the Arrhenius form, in terms of the temperature dependence of excess entropy,

\[
\eta = \eta_0 \exp \left( \frac{C}{T \cdot S_c} \right),
\]

where \( C \) and \( \eta_0 \) are constants. The liquid’s configurational entropy \( S_c \) is the entropy associated with the enormous number of configurational microstates, ("basins" on the energy landscape) to which the system gains access on fusion\(^{1,50,51}\) and which varies with temperature in proportion to the excess heat capacity of liquid over crystal.

Strictly, assessment of the configurational entropy \( S_c = S_{\text{liq}} - S_{\text{cryst}} \) requires knowledge of the entropy of liquid \( S_{\text{liq}} \) and vibrational entropy \( S_{\text{vib}} \). The latter cannot be directly measured. In practical data fitting, the excess entropy is commonly employed, \( S_{\text{ex}} = S_{\text{liq}} - S_{\text{cryst}} \), as an approximation of \( S_c \) by assuming \( S_{\text{vib}} = S_{\text{cryst}} \). This approximation assumes that the crystalline and liquid basins for thermal excitation have the same shape, which is, however, not generally expected. It has been shown in several cases,\(^{23}\) where data are available that \( S_c \) is proportional to \( S_{\text{ex}} \), i.e.,

\[
S_c \propto S_{\text{ex}}.
\]

Therefore, the Adam-Gibbs equation can describe viscosity equally well with total excess entropy \( S_{\text{ex}} \), replacing the total configurational entropy \( S_c \). It is common to calculate \( S_{\text{ex}} \) using

\[
S_{\text{ex}}(T_{\text{m}}) = \int \frac{C_p}{T} \, dT, \quad (T < T_{\text{m}}),
\]

\[
S_{\text{ex}}(T_{\text{m}}) + \int \frac{C_p}{T} \, dT, \quad (T > T_{\text{m}}),
\]

where the excess heat capacity is the difference between that of liquid and crystal, \( C_p = C_{p,\text{liq}} - C_{p,\text{cryst}} \), and \( S_{\text{ex}}(T_{\text{m}}) \) is the excess entropy at the equilibrium melting temperature \( T_{\text{m}} \). In the literature, the value of \( S_{\text{ex}}(T_{\text{m}}) \) is usually taken from entropy of fusion \( \Delta S_m \).

However, we must emphasize that, for melting of a eutectic composition, a temperature-independent “mixing”
entropy for the two crystals involved in the eutectic process should be taken into account. Thus, \( S_{ex}(T_m) \) should have the form

\[
S_{ex}(T_m) = \Delta S_m - \Delta S_{mix}. \tag{5}
\]

The entropy of fusion of Te\(_{85}\)Ge\(_{15}\) is obtained from the DSC melting peak (Fig. 2(b)) by \( \Delta S_m = \Delta H_m/T_e \approx 15.24 \text{ J mol}^{-1} \text{ K}^{-1} \). Ideal entropy of mixing can be used for \( \Delta S_{mix} \) (\( \Delta S_{mix} \approx 3.51 \text{ J mol}^{-1} \text{ K}^{-1} \)). Therefore, Eq. (5) yields \( S_{ex}(T_m) \approx 11.73 \text{ J mol}^{-1} \text{ K}^{-1} \). Figure 7(b) shows the total excess entropy \( S_{ex} \) (open rectangles) calculated from Eqs. (4) and (5). At the melting point, the \( \Delta S_m \) (solid star) is larger than \( S_{ex}(T_m) \).

The 2nd term in Eq. (4) can be obtained by integrating the excess heat capacity. Unlike water, the heat capacity of liquid Te\(_{85}\)Ge\(_{15}\) can be followed above a minimum down to \( T_g \) and the complete anomaly can be observed. The value of \( C_{p}^{\text{cryst}} \) is extrapolated above \( T_g \) using Kubaschewski equation,\(^4\) \( C_{p}^{\text{cryst}} = 3R + c'T + d'T^2 \), as shown dashed-line in Fig. 7(a). With \( C_{p}^{\text{cryst}} \) and data for Eq. (4), the Adam-Gibbs equation can be applied to the viscosity data.

Figure 8 shows the fitting results. The red line (B) is the Adam-Gibbs fit with a free pre-exponent \( \eta_0 \), which is found to be \( \eta_0 = 3.56 \times 10^{-5} \text{ Pa s} \), and \( C = 57.028 \text{ kJ mol}^{-1} \). If the pre-exponent \( \eta_0 \) is constrained to be compatible with the phonon cycle time (through the Maxwell relation \( \eta = G/\tau \) \( \eta_0 \approx 1 \times 10^{-5} \text{ Pa s} \), the fitted dashed line (A) yields the parameter \( C = 62.786 \text{ kJ mol}^{-1} \). Both fitted lines exhibit a “double-kink” corresponding to the onset and end of the heat capacity anomaly, although it is less distinct than the case derived for water.\(^4\) The Adam-Gibbs fits predict a course of viscosity below \( T_g \) down to that of a relaxor material, which is consistent with the high fragility of Te\(_{85}\)Ge\(_{15}\). The above analysis used entropy of fusion \( \Delta S_m \) as a constraining parameter to obtain the absolute values of \( S_{ex} \) by Eqs. (4) and (5). Alternative to Eq. (4), we can express \( S_{ex} \) as follows:

\[
S_{ex} = S_0 + \frac{\tau}{T_g} \int \frac{C_{ex}}{T} dT, \tag{6}
\]

where \( S_0 \) is a free fitting parameter, representing excess entropy at the starting temperature of integration, \( T_g \) (the end of the glass transition). By inserting Eq. (6) into the Adam-Gibbs equation and fitting the viscosity data, we obtain the fitting lines (see Fig. S1 in supplementary material\(^52\)) similar to that shown in Fig. 8 and a value of \( S_0 \). In doing so, \( S_{ex} \) can be derived from Eq. (6), agreeing well with that obtained from Eqs. (4) and (5) (solid line and open rectangles in Fig. 7(b)).

To quantify the fragility near \( T_g \), the data and fitted lines are re-plotted in the \( T_g \)-scaled Arrhenius plot (see Fig. 9), where it is compared with other related chalcogenide glass-forming systems. It appears that the low-temperature (near \( T_g \)) fragility of Te\(_{85}\)Ge\(_{15}\) is comparable to that of As\(_2\)Se\(_3\), As\(_2\)Te\(_3\), and Se, but much less fragile than that deduced from crystallization studies for the canonical phase-change memory composition Ge\(_2\)Sb\(_2\)Te\(_5\) (m ≈ 90).\(^23\) The m fragility of

FIG. 7. (a) The specific heat capacity of liquid Te\(_{85}\)Ge\(_{15}\) during cooling (data source: Ref. 48). A broad peak is observed around 630–750 K. The dashed line is a Kubaschewski fit for \( C_p \) of the crystalline state. The dotted-dashed line is the assumed “normal” component the liquid \( C_p \). (b) The excess entropy determined from Eqs. (4) and (5) using \( S_{ex}(T_m) \) is shown as open rectangles. The solid line is calculated from Eq. (6) by setting a free parameter \( S_0 = 5.16 \text{ J mol}^{-1} \text{ K}^{-1} \), which is obtained from the Adam-Gibbs fitting of the viscosity data in Fig. S1 (see supplementary material\(^52\)). The shaded area indicates two kinks in the excess entropy resulting from the \( C_p \) spike.

FIG. 8. Adam-Gibbs fits for the viscosity of Te\(_{85}\)Ge\(_{15}\) using the excess entropy \( S_{ex} \). (a) Lines A and B represent the fitting results using \( S_{ex} \) from Eqs. (4) and (5). Solid line (red) is obtained when pre-exponent is a free parameter while dashed line (cyan) is obtained when pre-exponent is constrained to the “universal” value \( 10^{-4} \text{ Pa s} \). The viscosity at \( T_g = 406 \text{ K} \) is set as \( 10^{12} \text{ Pa s} \) by convention. The heat capacity maximum results in a remarkable change in the temperature dependence of viscosity. Inset shows the zoom-in of the double-kink (arrows) region indicating a fragile-to-strong transition in the Adam-Gibbs extrapolated viscosity.
The glass transition of Ge bonding, suggesting no tetrahedral bonding in the liquid, in contrast to the case of water and silica. Rather, a picture of $p$-bonded liquid with atoms in octahedral environment was proposed. In this picture, at low temperature the octahedral local structure is distorted by a Peierls-like mechanism, while at high temperature the symmetry of structure is recovered. The driving force of removing Peierls distortion at high temperature was explained in terms of gain of vibrational entropy by Otjacques et al. Indeed, a gain in vibrational entropy consequent on some configurational rearrangement has been associated with an increase in fragility in other cases, where the excess entropy rather than the mere configurational entropy has been invoked as the important quantity on which to focus.

D. Fragile-strong transition, water-like phenomena, and their relevance to phase-change memory behaviors

This brings us to consideration of the switching alloys themselves to which so much attention has been given. Ge$_2$Sb$_2$Te$_5$, which (following Greer and coauthors) was, until very recently (see note added in proof), represented as fragile-continuous on the $T_g$-scaled Arrhenius plots as in Fig. 9, is more metallic in character than the composition on which we have focused attention so far. Several classes of metallic glass-formers have also been shown to have major differences in fragility between their high temperature stable liquid states, and their viscous liquid states near $T_g$. (Refs. 10 and 59) and a reversible fragile-to-strong transition has been documented in one case. There is, unfortunately, a wide “no-man’s land” between the melting point of Ge$_2$Sb$_2$Te$_5$ at 630°C and its (inconclusive) $T_g$ of 110°C, which can only be crossed with the help of the extreme cooling rates available to thin films in intimate contact with cold substrates, as in switching devices. The question of what sort of thermodynamic anomalies, reflecting liquid-liquid phase changes or the less extreme fragile-to-strong phase changes seen in the present study, might occur in this range is therefore very difficult to investigate. The nanocalorimetry studies of Greer and coauthors have only been able to observe the crystallization of the Ge bonding, suggesting no tetrahedral bonding in the system.

The entropy-temperature relation was continuous through the anomaly. In the case of water hyperquenched to the glassy state, experiments show that the configurational heat capacity that is left to lose at $T_g$ is extremely small, so there is a good possibility that the fragile-strong transition would be found discontinuous first order, if crystallization could be avoided.

What might be the structure-bonding changes to be associated with this fragile-strong transition? Besides the heat capacity on which we have focused attention, there have been companion studies of density and electrical resistivity anomalies in Te$_8$Ge$_{15}$ which have been attributed to structural changes in the liquid. Using ab initio molecular dynamics, Bichara et al. found no indication of $sp^3$ hybridization of the Ge bonding, suggesting no tetrahedral bonding in the system.
was reported in the DSC study of un-annealed hyper-quenched states of a variety of phase-change materials by Kalb et al.,\textsuperscript{63} which all show exothermic signals as the quenched (high enthalpy) state is relaxed. These exothermic relaxations are terminated in most cases by crystallization, as in water.\textsuperscript{64} Such behavior, compared with that of hyper-quenched glasses that do not crystallize,\textsuperscript{55,66} seems to imply a standard $T_e$ above the crystallization temperature which falls at $\sim 140^\circ$C in the case of Ge$_2$Sb$_2$Te$_5$, and $\sim 155^\circ$C in the case of Ge$_2$Sb$_2$Te$_5$. Evidence for an endothermic signal characteristic of the glass transition was obtained in one of the less rapidly crystallizing cases, AgIn–Sb$_2$Te, just before the crystallization.$^{63}$ Despite similar observations for water, which crystallizes at $\sim 155$ K, the preponderance of evidence and opinion places the glass transition temperature at water at the lower temperature of 136 K, so the question of the correct glass transition temperature for the phase-change materials should for the moment probably be left open.

A generous anonymous reviewer has made the following observation and invited us to incorporate it in this discussion. Since we agree with the ideas but previously felt we lacked the credentials to include them, we are now pleased to incorporate them by the following quotation: “Chalcogenide memory applications rely on (i) fast switching between glassy and crystalline states, in particular fast crystallization and (ii) stability of the memory-cell state (crystalline or glassy) over long periods. Systems showing a fragile-to-strong transition seem well adapted to meet these possibly conflicting requirements: the fragile liquid permits fast switching at higher temperatures, while the strong liquid and glass provide stability at lower temperatures.”

Whether or not fine capillary or microdroplet, techniques like those developed for the study of supercooled water, might reveal more interesting behavior in the supercooled state than has so far been reported, is a question to be considered for further work. The existence of amorphous phases of different density for Ge$_2$Sb$_2$Te$_5$ formed under different conditions (deposition, melt-quenching, or high-pressure) has been recorded.$^{65}$ It has also been noticed that the Clapeyron slope for this composition is negative$^{66}$ as for ice Ih. The study of meniscus behavior in a fine column of this composition in a quartz capillary tube would determine whether the liquid state of this composition might have a density maximum, and then a negative expansivity, as in water.

V. SUMMARY

Applying an analysis based on the Adam-Gibbs equation, we establish a link between the phenomenologies in viscosity and heat capacity anomalies of liquid Te$_6$Ge$_{15}$, and extrapolate the viscosity down to $T_e$. Although the viscosity at high temperature well above $T_e$ has a similar fragility of Ge$_2$Sb$_2$Te$_5$ ($m = 90$), the extrapolation near $T_e$ shows an intermediate liquid course ($m = 42–61$), demonstrating a fragile-to-strong transition in the liquid near $T_e$. The result of direct fragility measurement using DSC shows $m = 49 \pm 4$ (or 54.5 $\pm$ 3 in the case of area-matching method) near $T_e$, agreeing with the extrapolated values of $m$ ranging 42–61 with the preferred value 50. The fact that liquid Te$_6$Ge$_{15}$ is relatively strong compared with the highly fragile phase-change memory alloy Ge$_2$Sb$_2$Te$_5$ explains why crystallization of the former is much slower than the latter from the point of view of fragility. In addition to the extensive structural studies, liquid fragility is supported$^{62}$ as a key to understanding the mechanism of phase-change phenomenology for non-volatile random-access electronic memory applications.

Note added in proof

After this article was submitted, we learned of a paper by Greer and coworkers,$^{69}$ in press with Advanced Functional Materials that gives evidence for a fragile-to-strong crossover in a phase-change memory material, Ag-In-Sb-Te. While differently based from the present paper, their parallel observations and discussion substantiate the relevance of fragile-strong transition phenomenon to the understanding of phase-change random-access memory materials and their application.

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56See supplementary material at http://dx.doi.org/10.1063/1.4926791 for details of supplementary discussion and figures.


