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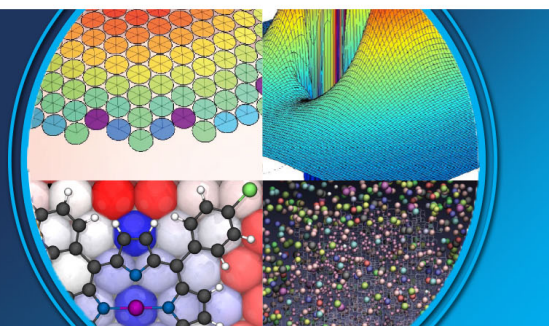
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PERSPECTIVES



From elemental tellurium to $\text{Ge}_2\text{Sb}_2\text{Te}_5$ melts: High temperature dynamic and relaxation properties in relationship with the possible fragile to strong transition

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We investigate the dynamic properties of Ge–Sb–Te phase change melts using first principles molecular dynamics with a special emphasis on the effect of tellurium composition on melt dynamics. From structural models and trajectories established previously [H. Flores-Ruiz *et al.*, Phys. Rev. B **92**, 134205 (2015)], we calculate the diffusion coefficients for the different species, the activation energies for diffusion, the Van Hove correlation, and the intermediate scattering functions able to substantiate the dynamics and relaxation behavior of the liquids as a function of temperature and composition that is also compared to experiment whenever possible. We find that the diffusion is mostly Arrhenius-like and that the addition of Ge/Sb atoms leads to a global decrease of the jump probability and to an increase in activated dynamics for diffusion. Relaxation behavior is analyzed and used in order to evaluate the possibility of a fragile to strong transition that is evidenced from the calculated high fragility ($M = 129$) of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ at high temperatures. *Published by AIP Publishing.*
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I. INTRODUCTION

Tellurides are considered as the most promising materials for phase change (PC) memory devices¹ and infrared transmitting waveguides.² In the former, the crystalline phase of a Te-based phase change material is heated above its melting point using an intense heating pulse and subsequently quenched into its amorphous state. The optical or electric contrast between both phases (crystalline vs. amorphous) is used for the applications, read by the appropriate device (e.g., a laser), and then permits to define the elementary bits for the data storage. One of the target materials having the best capabilities regarding phase change properties has been the chalcogenide Ge–Sb–Te ternary, and especially the compositional join defined by a pseudo-ternary line GeTe – Sb_2Te_3 .

The structural properties of the crystalline, liquid, and amorphous phases of such Ge–Sb–Te materials have been extensively studied,¹ both from theoretical and experimental viewpoints. Using different techniques (neutron diffraction, extended X-ray absorption fine structure, and X-ray absorption near edge structure), it could be shown that the liquid structures^{3–6} possess a defect octahedral local order for both Ge and Sb, whereas the densities of the amorphous and liquid phases were shown to be slightly lower than that of the crystalline phase. There have been also a large number of theoretical studies using density functional theory (DFT)-based simulations,^{5,7–11} and such studies have confirmed a certain number of experimental results such as the local octahedral structure of the liquid. Some of these conclusions are still debated in the literature,^{12–14} however. One of the reasons comes from a remaining numerical overestimation of the typical bond distances of Ge–Sb–Te materials, especially the

Ge–Te one, which has led to an important mismatch between the measured and calculated structure accessed, e.g., from diffraction studies. As a result, coordination numbers seem to be overestimated, at least when compared to alternative modeling schemes¹⁵ or, more recently, to spectroscopic data.¹⁶ In addition, such an insightful but still inaccurate simulation also affect the local base geometry of the Ge atoms, tetrahedral or defect octahedral,¹³ while also underestimating the intensity of the main peaks of the total structure factor.^{6,8} The issue of the base geometry appears to be central for the understanding of the PC mechanism given that such typical structural motifs involve different chemical bondings while also requiring the participation of different electronic orbitals. This crucial issue has recently been solved by including dispersion forces into the DFT-based molecular dynamics simulations, and different applications on liquid Ge–Sb–Te,¹⁷ Ge–Te^{18–20} and amorphous Ge–Te¹³ have, indeed, indicated that a substantial improvement of the simulated structural properties can be achieved when van der Waals corrections are added to the treatment of the interatomic interaction. As a result, it could be shown that the fraction of tetrahedra is much larger in tellurides so that Ge–Te displays some similarities with Ge–Se, except the larger crystallization tendency. Such corrected DFT investigations have been also performed for the corresponding crystalline phase.^{21,22}

Having improved the structural description (Fig. 1), one may wonder how the dynamics of such more realistic phase change liquids behave. This is the purpose of the present contribution which focuses on the dynamics and the relaxation of $\text{Ge}_x\text{Sb}_x\text{Te}_{100-2x}$ melts with changing cross-linking (Ge, Sb) content x , including $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225). One expects

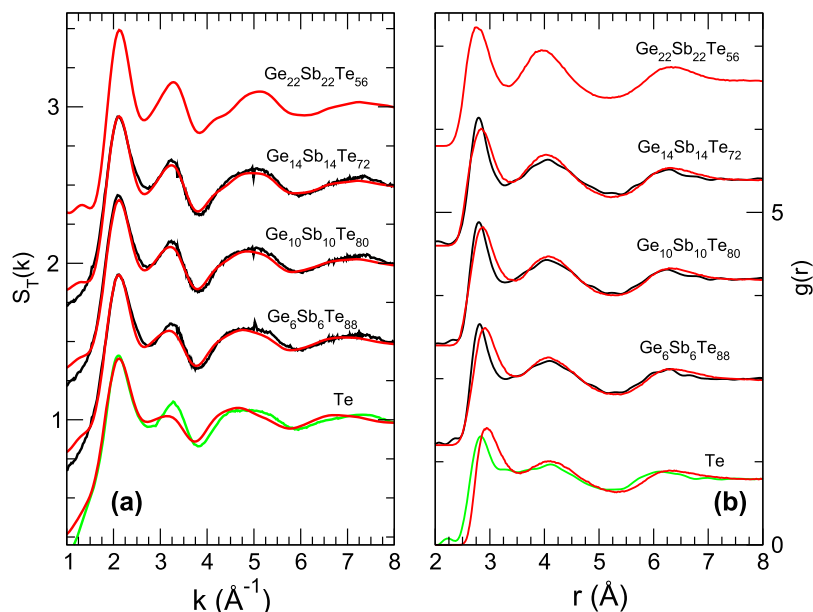


FIG. 1. Calculated¹⁷ (red curves) static structure factors $S(k)$ (a) and pair correlation function $g(r)$ (b) for the investigated compositions at 820 K and comparison with experimental neutron diffraction results: elemental Te (green curves)⁶⁴ and Ge–Sb–Te liquids (black curves). Adapted from Ref. 17.

from such systematic studies to derive a trend between Te and GST225 that might help to clarify certain issues related to dynamics. In fact, the temperature dependence of diffusivity and viscosity is important for nucleation and growth of the crystalline phases and, hence, for the PC applications.¹ In addition, given the high crystallization tendency^{23,24} of such telluride liquids such as GST225, $\text{Ge}_1\text{Sb}_2\text{Te}_4$, or $\text{Ag}_4\text{In}_3\text{Sb}_{67}\text{Te}_{26}$ (AIST), the entire dynamics of the supercooled metastable state can be barely probed so that molecular simulations can shed some light on aspects of liquid relaxation and viscosity.

The present investigation is also guided by other motivations. Dynamic anomalies have been detected in network glass-forming liquids with increasing connectedness,^{25–27} and for chalcogenide materials, these anomalies have been found to be linked with the way the viscosity (η) or the relaxation time (τ_α) towards thermodynamic equilibrium evolves with temperature. The behavior of η and τ_α with temperature is usually quantified by a fragility index²⁸ defined by

$$\mathcal{M} \equiv \left[\frac{d \log_{10} \tau}{dT_g/T} \right]_{T=T_g} \quad (1)$$

and leading for large $\mathcal{M}$ (termed as fragile liquids) to a curvature in an appropriate plot²⁸ ($\log_{10} \eta$ or $\log_{10} \tau$ with T_g/T). Here, T_g is the glass (reference) temperature at which one has $\log_{10} \eta = 12$. For the particular GST225 composition, differential scanning calorimetry (DSC) across the glass transition have permitted access to the liquid fragility²⁹ and have revealed that this archetypal PC material is fragile ($\mathcal{M} = 90$) although there are some uncertainties regarding the measure of $\mathcal{M}$ in tellurides given the experimental challenge.^{30,31} For instance, the fragility of $\text{Ge}_{15}\text{Te}_{85}$ was found between $\mathcal{M} = 42$ ⁵⁰ and $\mathcal{M} = 120$,³³ the experimental discrepancies being, apparently, based on the measurement methods (see Ref. 50 for discussion). For sulfur- or selenium-based liquids, fragility minima are observed with composition^{34,35} and are usually linked with an anomalous relaxation³⁶ and the onset of a rigid network structure^{37,38} found at a flexible to rigid transition. This induces

a series of other anomalous behaviors observed in the glass transition region such as minimal enthalpic changes across the glass transition,³⁹ space-filling tendencies,^{40,41} weak ageing phenomena,⁴² and vibrational thresholds.⁴³ Some of these features are important for the optimization of the PC properties as recently emphasized for $\text{Ge}_x\text{Te}_{1-x}$. For instance, it was shown that both structural motifs⁴⁴ responsible for a Ge-rich nanoscale phase separation and the resistance drift involved in ageing phenomena⁴⁵ could be linked with aspects of network rigidity. And since the presence of Ge–Ge bonds favours the presence of tetrahedra,¹² the full understanding of the combined effect of homopolar bonding, geometry, rigidity, and dynamics is very much desirable.

A recent numerical investigation on a parent liquid ($\text{Ge}_x\text{Se}_{1-x}$) has shown that such fragility anomalies are linked with the spatial distribution of atomic radial and angular interactions able to constrain the network structure.³⁸ Although signatures of a flexible to rigid transition have been observed in different amorphous tellurides,^{46–50} the experimental detection of dynamic anomalies in corresponding liquids appears to be less evident because of the increased crystallization tendency in the supercooled state, a problematic definition of relevant (bending and stretching) interactions due to the partially unknown local geometries (octahedral vs tetrahedral), and the strong temperature dependence of the coordination numbers.^{8,9,17,20} Furthermore, corresponding experimental data are sparse. However, an MD-based enumeration of topological constraints in amorphous Ge–Sb–Te materials has been able to clarify this issue and has led to the identification of a mean-field flexible to rigid transition line close to the SbTe_4 – GeTe_4 join⁵¹ separating two regions in the Te-rich part of the phase diagram. The choice to concentrate on the compositional line $\text{Ge}_x\text{Sb}_x\text{Te}_{1-2x}$ is, therefore, also motivated by these recent results regarding rigidity because of a possible flexible to rigid transition for the $\text{Ge}_{10}\text{Sb}_{10}\text{Te}_{80}$ composition.

Studies in the liquid state have also emphasized the particular behavior of viscosity in binary and ternary telluride liquids

which underscores a possible strong to fragile transition^{52,53} with temperature. Here, the viscosity is supposed to change more or less suddenly by several orders of magnitude, and such a transition has been revealed from a careful series of viscosity measurements in the parent liquid $\text{Ge}_{15}\text{Te}_{85}$.³² These intriguing findings have been rationalized in terms of a semiconductor to metallic transition supposed to influence the crystallization kinetics^{32,50} below the liquid surface, although some of the driving phenomena, e.g., hidden liquid-liquid transitions, remain disputed and probably require more investigations on model systems as recently performed with success on liquid silica.^{54,55}

Here, using the Grimme-corrected DFT simulations, we investigate as a function of Te content the diffusivity and the relaxation properties of $\text{Ge}_x\text{Sb}_x\text{Te}_{100-2x}$ liquids that crosses the pseudo-ternary line Sb_2Te_3 – GeTe , while also replacing Ge/Sb in the Te-based materials in an equivalent fashion between elemental Te and $\text{Ge}_2\text{Sb}_2\text{Te}_5$. Results show that the increase of cross-linking elements (Ge, Sb) globally reduces the dynamic behavior with a global reduction of the diffusivities with increasing cross-link density. Corresponding activation energies do not seem to indicate a signature of dynamic anomalies.³⁸ The models lead to estimated viscosities that are globally compatible with experimental results and previous simulations. We then analyze the relaxation properties and find an Arrhenius dependence for the relaxation time that permits one to probe the possibility of a fragile to strong transition, and because of a large difference in liquid fragilities between the low- and high-temperature liquids, for GST225, such a transition is identified close to the melting point at $T_s = 792$ K.

This paper is organized as follows. Section II describes the computational methods used for this study. We will then focus on the results on the dynamics such as diffusivity and Van Hove correlation functions able to substantiate the properties of the diffusing atoms. We address the issue of relaxation by focusing on the intermediate scattering function and related quantities that can be extracted from its time evolution. In Sec. IV, we will discuss the results, contrast the findings with experiments, and discuss the fragile to strong transition of the telluride melts from the determination of the relaxation time with temperature and composition. Finally, we summarize the main findings and draw some conclusions.

II. NUMERICAL METHODS

Five compositions $\text{Ge}_x\text{Sb}_x\text{Te}_{100-x}$ ($x = 0\%$, 6% , 10% , 14% , 22%) have been investigated from first principles molecular dynamics simulations in NVT ensemble. 300 atoms have been positioned in a periodically repeated cubic cell whose size has been adapted to recover measured experimental densities at given temperatures.¹⁷ The electronic structure has been described within DFT and has evolved self-consistently during the motion.⁵⁶ A generalized gradient approximation (GGA) has been used, based on an improved scheme for the exchange-correlation energy obtained by Perdew, Burke, and Ernzerhof (PBEsol). This functional has been found to improve substantially the structural description of elemental tellurium in the liquid phase.⁶⁴

Valence electrons were treated explicitly, in conjunction with Trouiller-Martins norm conserving pseudopotentials.⁵⁷ The wave functions have been expanded at the Γ point of the supercell on a plane wave basis set with an energy cutoff $E_c = 20$ Ry. During the Car-Parrinello Molecular Dynamics (CPMD) simulation, a fictitious electron mass of 2000 a.u. and a time step of $\Delta t = 0.12$ fs have been used to integrate the equations of motion. Temperature control has been implemented for both the ionic and electronic degrees of freedom by using Nosé-Hoover thermostats⁵⁸ with a frequency of 800 cm^{-1} . An attractive dispersion correction proposed by Grimme⁵⁹ has been used and leads to a substantial improvement of the structural description (Fig. 1) in both Ge–Te and Ge–Sb–Te melts.^{17,20} Corresponding Grimme parameters are given in Ref. 17.

The starting configuration of all liquids is a random structure of Ge, Sb, and Te atoms fulfilling the corresponding stoichiometries. Loss of the memory of the initial configurations has been achieved through preliminary runs at 2000 K over 50 ps at densities corresponding to a high temperature extrapolation of the experimental densities. The total simulation time of these preliminary runs induces mean square displacements of the order of several cell lengths which provide a good indication that the memory of the initial configurations has been lost. After equilibrating at different target temperatures (1800 K, 1500 K, 1200 K, 820 K, and 743 K), trajectories for each compositions/temperatures have been accumulated over 25–30 ps each and used for the analysis of the dynamic properties. The lower temperature clearly corresponds to the supercooled liquid region given the, e.g., measured glass transition temperatures of $T_g = 383$ – 430 K^{24,60} and melting temperatures $T_m = 900$ K¹ for GST225 and $T_g = 340$ K for elemental Te.⁴⁴

III. RESULTS

A. Diffusion

We first compute the mean-square displacement of an atom of type α in the melt given by

$$\langle r^2(t) \rangle = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle \quad (2)$$

and extract from the dependence of $\langle r^2(t) \rangle$ the long time behavior where the dynamics becomes diffusive. Figure 2 shows such a behavior and indicates that, e.g., Te atoms are diffusive even for the lowest considered liquid temperature (820 K) because $\langle r^2(t) \rangle$ obviously has a slope of 1 for $t > 10$ ps in a log-log plot and one still has $\langle r^2(t) \rangle$ of about $10\text{ \AA}^2$. Using the Einstein relation at long time $\lim_{t \rightarrow \infty} \langle r^2(t) \rangle / 6t = D$, the diffusion constants D for various species can be calculated from the mean square displacement as a function of composition and temperature.

Corresponding results are represented in Fig. 3 for the different compositions and exhibit an Arrhenius-like dependence $\exp[-E_A/T]$ as already found for a variety of oxide or chalcogenide melts.^{27,61–63}

These can be compared to experimental or other numerical available data [Fig. 4(a)]. For liquid tellurium, it is seen that our calculated diffusivities are very close to those calculated from a

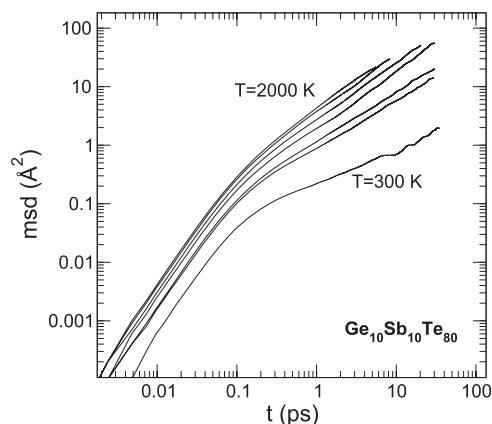


FIG. 2. Tellurium mean-square displacement of a $\text{Ge}_{10}\text{Sb}_{10}\text{Te}_{80}$ liquid at different temperatures. Note the onset of the diffusive régime at $\approx 2\text{-}5$ ps at a high temperature ($T \geq 1200$ K).

different electronic scheme (Tao, Perdew, Staroverov, Scusera (TPSS)⁶⁴), i.e., we find $1.83 \times 10^{-5} \text{ cm}^2/\text{s}$ for 820 K, to be compared with $4.62 \times 10^{-5} \text{ cm}^2$ at 970 K.⁶⁴ Differences in diffusivities due to the exchange-correlation functional have been acknowledged in lighter chalcogenides, and it has been found that these were essentially driven by changes in the local structure and coordination number.^{67,68} Given that there are slight differences between the present simulated liquid Te and the one using the TPSS functional, we conjecture that these may arise from a small difference in structure (i.e., $g(r)$) although the coordination number of Te was about to be the same ($n_{\text{Te}} = 2.40$ for 910 K¹⁷ and 970 K⁶⁴).

Both simulation schemes are actually very close to the only reported experimental data point⁶⁵ of liquid Te measured at 720 K [see Fig. 4(a)]. The numerical results can also be compared with values extracted from a Stokes-Einstein estimate of diffusivities from viscosity data^{66,69,70} (see below) and results are found to agree, at least at low temperatures (820 K). The effect of the addition of Ge and Sb atoms leads to a strong decrease of diffusivities as the temperature is reduced [Figs. 3 and 4(a)], a feature that has been already noticed and which

signals the slowing down of the dynamics as the density of cross-links increases or the temperature decreases.^{36,38} In the present case, the diffusivities decrease by an order of magnitude as the liquid is cooled from 1500 K down to 820 K. At high temperatures (1500 K, i.e., $T > T_m$), all liquids behave similarly and effects of composition on transport properties are weak. From Fig. 4(a), one can detect, indeed, that for $T > 1200$ K, there are minor differences in the diffusion constant D_{Te} between Te and GST225, both being in the liquid state ($T_m = 722$ K and 900 K, respectively¹). However, we also note that the strongest reduction of diffusivities is found between the 14% and the 22% (GST225) liquid (Fig. 3). The present results are also consistent with a recent study on liquid GST225. We find, indeed, $D_{\text{Ge}} = 7.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 823 K, the latter value being similar to the one determined by Schumacher *et al.* at 852 K.⁶⁹

For the GST225, corresponding activation energies E_A calculated from Fig. 4(a) are found to be of about 0.30 eV, 0.26 eV, and 0.29 eV for germanium, antimony, and tellurium, respectively. These numbers compare rather well with those determined in other typical PC liquids. In liquid GeTe, Liu *et al.*⁷² have found from a combination of *ab initio* simulations and classical crystallization theory $E_A = 0.30$ eV and $E_A = 0.32$ eV for Ge and Te, respectively. These are also consistent with diffusivity results⁶⁹ determined from similar simulations for liquid $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ($E_A = 0.256$ eV) and experiments on viscosity ($E_A = 0.266$ eV) but also with typical values found for Sb_4Te (0.30 eV).⁷³

In order to further check if the present diffusivity results are consistent and given that a direct calculation of a Green-Kubo viscosity is out of reach because of limitation in time and system size, we use the following Stokes-Einstein (SE) relationship to determine the liquid viscosities:

$$\eta = \frac{k_B T}{6\pi R D}, \quad (3)$$

where D is the calculated average diffusivity and R is a typical distance responsible for viscous flow (a hydrodynamic radius). Note that one may use the alternative Eyring

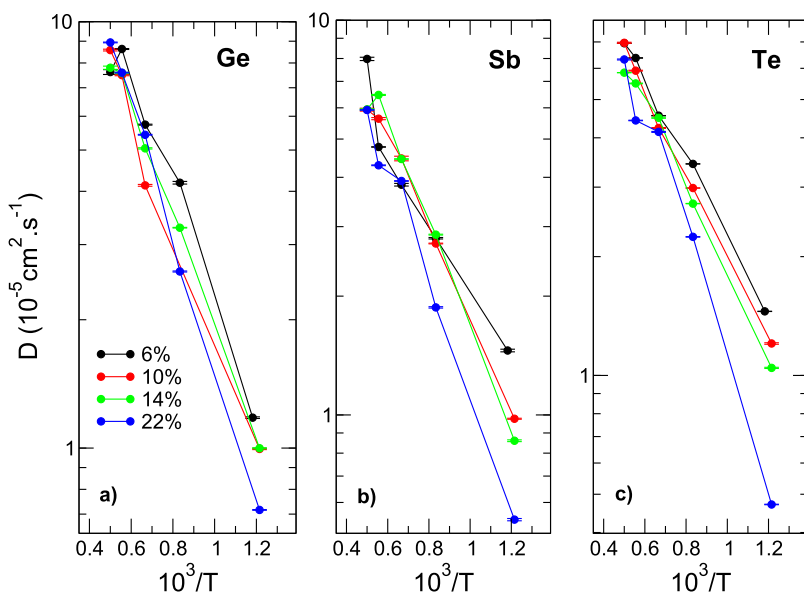


FIG. 3. Arrhenius plot of Ge (a), Sb (b), and Te (c) diffusivities as a function of inverse temperature.

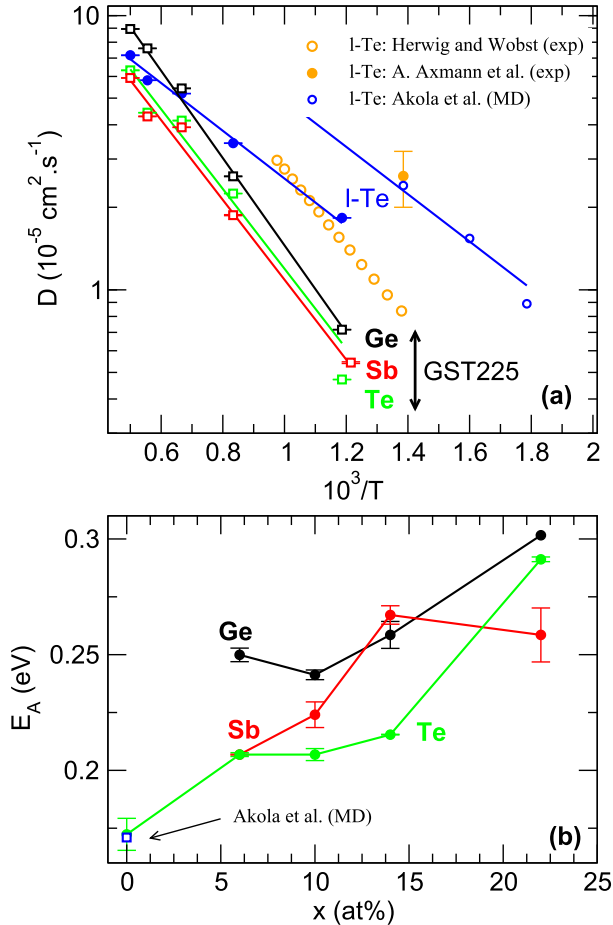


FIG. 4. (a) Arrhenius plot of the self-diffusion constant in liquid Te [blue filled circles, same as data in Fig. 3(c)] and Ge (black open squares), Sb (red open squares), and Te (green open squares) in liquid $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225). The liquid data for Te can be compared to similar simulations using a different electronic scheme (open blue circles, Akola *et al.*⁶⁴), to an experimental data point from quasielastic neutron scattering (orange, Axmann *et al.*⁶⁵), and to viscosity based diffusivities from Herwig and Wobst⁶⁶ [see Eq. (3)]. (b) Determined activation energies E_A as a function of Ge/Sb content. Comparison with the activation energy (open blue square) calculated for liquid Te by Akola *et al.*⁶⁴

equation which also behaves as $\eta \approx T/D$. Values for R correspond to the interatomic Ge–Te distance, but it can also be more simply determined from $2R = \rho^{-1/3}$ (with ρ the liquid density) which gives a rather good reproduction of viscosity data from diffusivity calculations in different chalcogenide liquids.^{36,74} Corresponding results using Eq. (3) are displayed in Fig. 5, together with experimental^{66,69,70} and numerical results,^{64,69} and these appear to be consistent. At high temperatures, the similar diffusivities (Fig. 4) lead to values for η that are close (they differ by a slight change due to density), and η starts to increase substantially in the region $800 \text{ K} < T < 1100 \text{ K}$ only, as also acknowledged in experimental measurements. Here, one notices that for the same temperature, a marked effect of composition leads to an increase of the GST225 viscosity, i.e., by a factor of 3–4 with respect to liquid tellurium.

B. Van Hove correlations

Additional insight of the diffusive motion is provided by the Van Hove correlation function^{75,76} which is a density-time

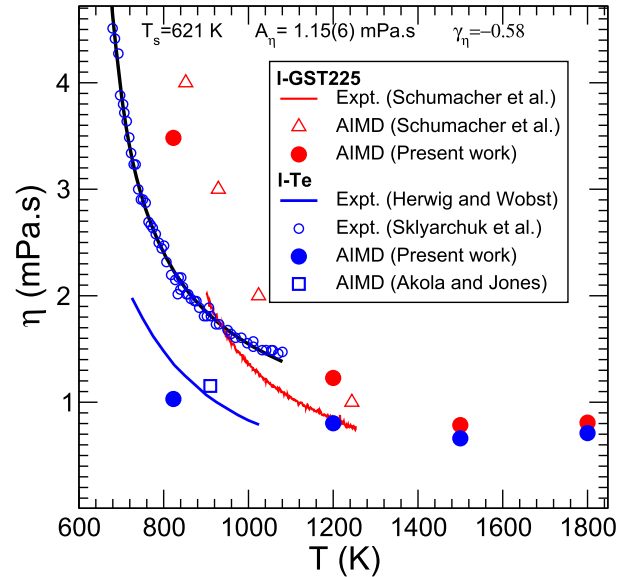


FIG. 5. Estimated SE viscosity as a function of temperature (filled circles) compared to previous results from molecular simulations (Schumacher *et al.*, red open triangles;⁶⁹ Akola and Jones, red open square⁶⁴) and experimental measurements (solid lines) from the studies of Schumacher *et al.*,⁶⁹ Wobst and Herwig,⁶⁶ and Sklyarchuk *et al.*⁷⁰ for GST225 and Te. The solid black line represents a Speedy-Angell fit⁷¹ for the Te data⁷⁰ and corresponding parameters are given at the top. See the text for details.

correlation of particles and permits to quantify correlated real space dynamics, while also being able to characterize certain transport mechanisms. Given that there is a particle at the origin at time $t = 0$, the Van Hove correlation for species α is usually given as

$$G^\alpha(\mathbf{r}, t) = \frac{1}{N_\alpha} \left\langle \sum_{i=1}^{N_\alpha} \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)) \right\rangle, \quad (4)$$

where $\langle \cdot \rangle$ denote the ensemble average. The Van Hove correlation function can be divided into a self-part and a distinct part for the cases $i = j$ and $i \neq j$, respectively. The former gives an indication about an average motion whereas the latter is directly related to unlike particle correlations that reduces to the static pair correlation function $g(r)$ at $t = 0$.⁸⁰ For the self-part, the probability of finding a particle of species α at the position $\mathbf{r}$ at time t is given by

$$4\pi r^2 G_s^\alpha(r, t) = \frac{1}{N_\alpha} \left\langle \sum_{i=1}^{N_\alpha} \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)) \right\rangle, \quad (5)$$

and $4\pi r^2$ results from the spherical integration of an isotropic media. Figure 6 now exhibits the self-part of the Van Hove correlation function $G_s^\alpha(r, t)$ after 20 ps for 820 K.

Results are shown in Fig. 6 which displays for each species the Van Hove distribution at the lowest investigated temperature (820 K). We obtain for $G_s^\alpha(r, t)$ a global shift to lower distances r as the (Ge, Sb) composition x is increased which leads to a global reduction of the atomic jump probability (inset of Fig. 6) so that only $\approx 20\%$ atoms move by a typical atomic distance of $2.47 \text{ \AA}$ at 820 K. In parallel, the average jump distance decreases in a similar fashion, from, e.g., $4.33 \text{ \AA}$ in liquid Te down to $2.20 \text{ \AA}$ at 22% (GST225) for the Te atoms. Although

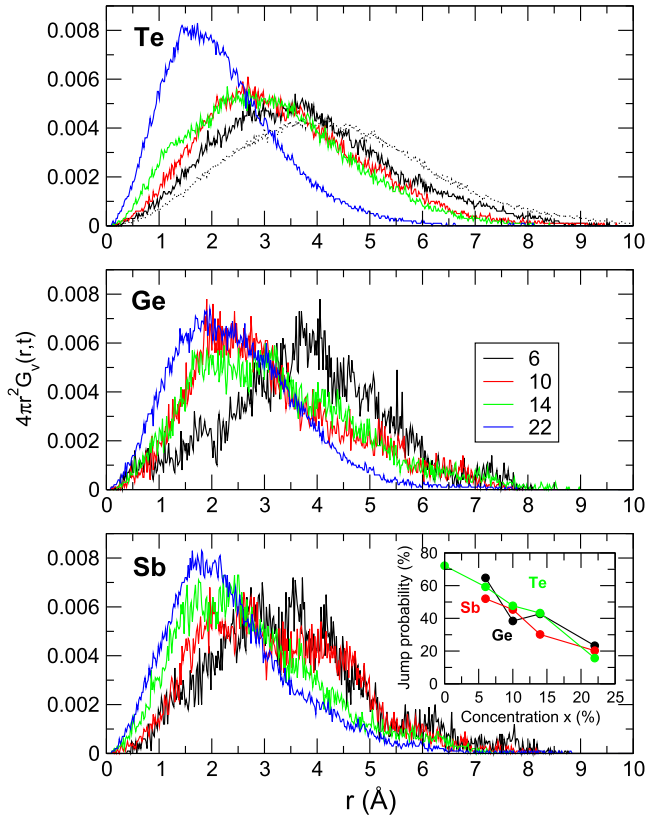


FIG. 6. Van Hove correlation function $4\pi r^2 G_v^\alpha(r, t)$ at 820 K at $t = 20$ ps for the different species (Te, Ge, Sb). The dotted line in the top panel corresponds to the liquid Te. The inset in the lower panel represents the probability that an atom jumps by a distance larger than $r_{min} = 2.47$ Å at 820 K.

the Ge statistics is small for the 6% system ($\text{Ge}_6\text{Sb}_6\text{Te}_{84}$, 18 atoms) and leads to a more noisy function, one clearly notes that the dynamic behavior of this liquid is rather different for $G_s^{\text{Ge}}(r, t)$ and $G_s^{\text{Sb}}(r, t)$ given that both display a tail at larger distances (4-5 Å) which is an indication of a departure from Fickian dynamics⁷⁷ that behaves as $G_s^\alpha(r, t) = \exp[-r^2/Dt]$. This tail is a signature of some cooperative motion (it usually builds up as the liquid becomes more and more viscous). This situation contrasts with the profile of $G_s^\alpha(r, t)$ found for the other compositions, whereas $G_s^{\text{Sb}}(r, t)$ appears to be somewhat intermediate for both $\text{Ge}_6\text{Sb}_6\text{Te}_{88}$ and $\text{Ge}_{10}\text{Sb}_{10}\text{Te}_{80}$.

The maximum of $4\pi r^2 G_s^\alpha(r, t)$ can be related to diffusion processes in liquids and solids and reveals that the most probable distances involved in the jump processes (2-3 Å) are those corresponding to first neighbour distances or second neighbour distances to the best. This is a strong indication that diffusive processes are governed at such high temperatures by the motion of single atoms, a situation that is particularly met for the Te atoms for which $4\pi r^2 G_s^\alpha(r, t)$ has a nearly similar shape for all compositions except GST225.

C. Relaxation

We now investigate the relaxation behavior of $\text{Ge}_x\text{Sb}_x\text{Te}_{1-2x}$ liquids by examining the intermediate scattering function which is a quantity usually accessed from X-ray or neutron scattering^{78,79} and permits one to follow the decay of density fluctuations with time and turns out to be a useful

property for the investigation of glassy relaxation. From MD simulations, the self-intermediate scattering function $F_s^\alpha(k, t)$ for the species α can be calculated and is equal to

$$F_s^\alpha(k, t) = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} \exp(i\mathbf{k} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))), \quad (6)$$

which is also defined as the Fourier transform⁸⁰ of the Van Hove correlation function defined in Eq. (5). In Fig. 7, we represent the wave vector dependence of $F_s(k, t)$ for a given composition (GST225) at different wave vectors including $k = k_{max} = 2.13$ Å⁻¹ that corresponds to the position¹⁷ of the principal peak in the static structure factor $S(k)$ (Fig. 1). $F_s(k, t)$ displays some salient features that are obtained for a variety of typical glass-forming systems,^{36,37,81,82} and these are recovered for the present Ge–Sb–Te liquids. At higher temperatures (e.g., 1500 K), the relaxation process takes place in a single step Debye-like fashion³⁶ (not shown), and one can fit $F_s(k, t)$ with a simple exponential decay ($e^{-t/\tau}$), where τ represents the structural relaxation time towards thermal equilibrium at which one has $F_s(k, t) \approx 0$. However, as the system becomes more viscous and exhibits a progressive glassy behavior (820 K corresponds to $T_g/T = 0.52$, with $T_g = 430$ K²⁹), a typical β -relaxation plateau builds up at intermediate times,⁸³ and this plateau extends to very long times and becomes of the order of the simulation time for 300 K. For intermediate temperatures and sufficiently long simulation time however, the decay of $F_s(k, t)$ to zero is visible and characterizes the α -relaxation régime of the liquid.⁸⁴

At the lowest liquid temperature (820 K), one can notice that for typical structural correlations involved in short distances (2.13 Å⁻¹ and 3.73 Å⁻¹), a full relaxation to equilibrium is achieved on the 20-30 ps time scale, and $F_s(k, t)$ becomes close to zero. The situation contrasts with the one found for $k = 1.07$ Å⁻¹ which shows only a partial relaxation given that the wavevector corresponds to correlations found at intermediate length scales, typical of the first sharp diffraction peak⁸⁶ observed at lower temperatures, and such correlations need longer times to decay to zero.

Finally, in Fig. 8, we show the function $F_s(k_{max}, t)$ for $k_{max} = 2.13$ Å⁻¹ for the different 820 K liquids for the three

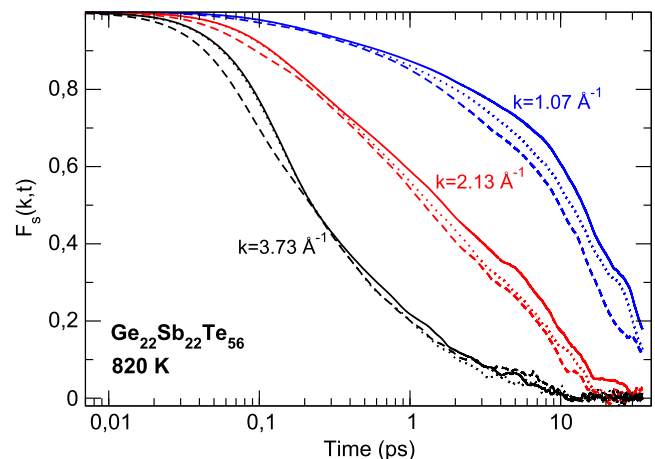


FIG. 7. Reciprocal space vector dependence of $F_s(k, t)$ of $\text{Ge}_{22}\text{Sb}_{22}\text{Te}_{56}$ (GST225) at 820 K for Te (solid curves), Sb (dotted curves), and Ge (broken curves) at different wave vectors k .

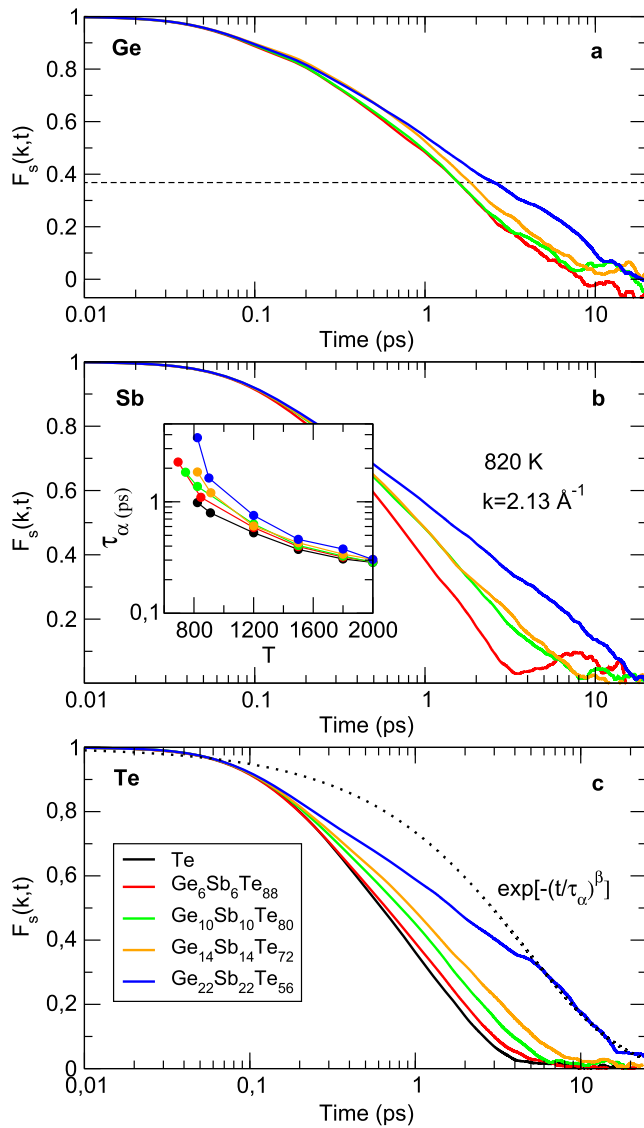


FIG. 8. Self-part of intermediate scattering function $F_s(k, t)$ of Ge (a), Sb (b), and Te (c) at 820 K and $k = 2.13 \text{ \AA}^{-1}$ for the compositions of interest. The horizontal solid line in (a) corresponds to the value e^{-1} , whereas the broken line in (c) shows the Kohlrausch-Williams-Watts (KWW) fit at the long time limit of $F_s(k, t)$ for $\text{Ge}_{22}\text{Sb}_{22}\text{Te}_{56}$ (GST225). The inset shows the calculated relaxation time τ_α as a function of temperature for all Ge–Sb–Te melts.

species (Te, Ge, Sb). It is seen that there is an enhanced slowing down of the relaxation in the GST225 liquid that obviously exhibits a slower dynamics and $F_s(k, t)$ is shifted to longer times, leading even to the emergence of a short β -relaxation régime that is especially visible for Te species [Fig. 8(c)]. For times which are typical such⁸² as $F_s(k_{\text{max}}, t) < 1/e$, one can fit the intermediate scattering function with a stretched Kohlrausch-Williams-Watts (KWW) exponential decay $\exp[-(t/\tau_\alpha)^\beta]$, with τ_α being the structural relaxation time and β being the Kohlrausch exponent.⁸⁵ The value of $\beta < 1$ indicates that the decay of the spatial density correlations extends over a wide range in time^{36,78,79,85} and signals that the relaxation cannot be described by a simple exponential Debye relaxation. The analysis on the relaxation times as a function of composition and temperature at the selected $k = 2.1 \text{ \AA}^{-1}$ is summarized in the inset of Fig. 8. With increasing cross-linking Ge/Sb elements, the relaxation time increases

markedly at low temperatures with a growth of a factor of four between 800 K and approximately 1000 K. The results for τ_α obtained from the KWW fit are actually compatible with the simple estimate $F_s(k, \tau_\alpha) = 1/e$ that is also used in the literature.^{81,82} For instance, we find that for the liquid $\text{Ge}_6\text{Sb}_6\text{Te}_{88}$ at 820 K, $\tau_\alpha = 1.67(4)$ ps from a KWW fit and $\tau_\alpha = 1.57(5)$ ps from the condition $F_s(k, \tau_\alpha) = 1/e$.

IV. DISCUSSION

The obtained numerical results can now be put in perspective with respect to previous studies on Ge–Sb–Te melts or parent systems and connected to the topics presented in the Introduction.

A. Fragile to strong transition

In order to investigate the possibility of a fragile to strong transition, we use the calculated relaxation times τ_α with temperature and composition (inset of Fig. 8) in order to infer the nature of the dynamics at high temperatures for $T \geq 820$ K. Figure 9 shows the data in an Angell plot, i.e., we represent $\log_{10} \tau_\alpha$ as a function of T_g/T . Here, we have used the glass transition $T_g = 343$ K for elemental tellurium and 430 K for GST225,²⁹ assuming a linear increase between $x = 0\%$ and 22% in order to rescale the behavior at the intermediate compositions (6%, 10%, and 14%) with appropriate glass transition temperatures. Such an increase of T_g with liquid connectivity has been found in binary Si–Te⁸⁷ and Ge–Te^{44,88} glasses and turns out to be much less important when compared to lighter chalcogenides,^{34,35} as also recently emphasized.³² Results show a weak variation with composition for such ternary telluride melts over the reduced temperature range (T_g/T) between 0.2 and 0.6 (Fig. 9). The variation of τ_α parallels the one of experimental viscosity data⁶⁹ (right axis) which permits to estimate a

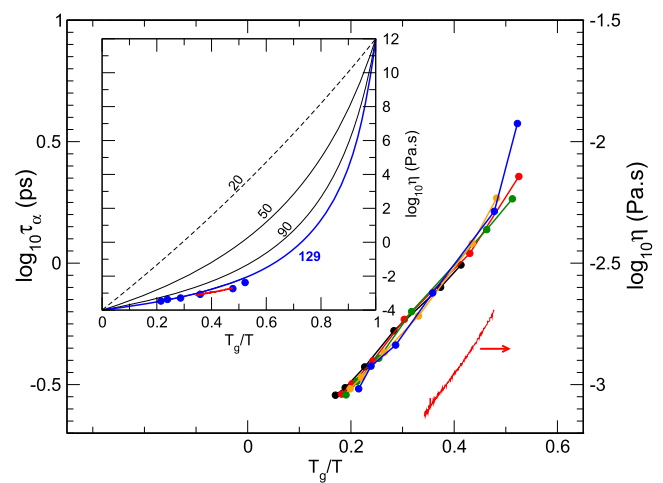


FIG. 9. Representation in an Angell plot of τ_α (same data as inset of Fig. 8(b)) together with the viscosity data from the work of Schumacher *et al.*⁶⁹ (red curve, right axis). The inset shows a prediction of viscosity η from τ_α as a function of T_g/T for GST225 (blue symbols) together with the experimental data (red,⁶⁹ same as the main panel). A VFT fit ($M = 129$) to the data is given (blue curve), together with VFT plots ($\log_{10} \eta_\infty = -4$) at different fragilities, taken from the studies of Orava *et al.*²⁹ ($M = 90$) for GST225 and Wei *et al.*³² ($M = 50$) for $\text{Ge}_{15}\text{Te}_{85}$. These serve for comparison.

nearly temperature-independent infinite frequency shear modulus given that one has $\eta = G_\infty \tau_\alpha$, and we find $G_\infty = 3.4 \times 10^{12}$ GPa, a value that is close to those usually found in supercooled liquids.⁸⁴

Using this determined value of G_∞ , we now represent a τ_α -based viscosity as a function of T_g/T (inset of Fig. 9) that also agrees with viscosities estimated from the diffusivity via Eq. (3). It is important to notice that in the region $0.2 \leq T_g/T \leq 0.6$, both τ_α -based and measured⁶⁹ viscosities display rather low values for η , of the order of mPa s. These are compatible with the possibility of a fragile to strong transition given that a low temperature calorimetric measurement²⁹ close to the glass transition that has given a fragility of $\mathcal{M} = 90$ which leads to a curve for $\eta(T)$ (black curve in the inset) that can hardly fit our represented data across the whole temperature range. A fit to the τ_α -based viscosity data using a Vogel-Fulcher-Tamman (VFT) can be performed. Here, one uses the form which involves explicitly⁸⁴ the fragility $\mathcal{M}$ and the glass transition temperature T_g ,

$$\log_{10} \eta(T) = \log_{10} \eta_\infty + \frac{(12 - \log_{10} \eta_\infty)^2}{\mathcal{M}(T/T_g - 1) + (12 - \log_{10} \eta_\infty)}, \quad (7)$$

which leads to $\mathcal{M} = 129$ if the constraint $\log_{10} \eta_\infty = -4$ is applied for the high temperature viscosity and $\mathcal{M} = 180$ otherwise. In this case, one has $\log_{10} \eta_\infty = -3.82$ which is still compatible with typical values for the melt viscosity at very high temperatures^{89,90} and close, in fact, to the proposed limiting viscosity of $\eta_\infty = 10^{-4}$ Pa s⁹¹ that we have fixed at the first stage of the fitting procedure. A fit to the experimental viscosity data is given in Subsection IV B. An alternative fitting scheme builds on the Mauro-Yue-Ellison-Gupta-Allen (MYEGA) form⁹¹ which can be extended for the special case of fragile to strong transition to a double exponential expression⁹² using five parameters. Given the limited number of data points obtained from the simulations (six), the use of such a fitting expression appears rather risky. Whatever the method used, one realizes that just below the melting temperature ($T_g/T_m = 0.478$), the supercooled liquid is extremely fragile; this statement being true for all ternary compositions. Similarly, a VFT fit to the liquid data⁷⁰ leads for liquid Te to $\mathcal{M} = 50$ and $T_g = 307$ K, i.e., close to the limiting ($x = 0$) value found in $\text{Ge}_x\text{Te}_{1-x}$ glasses (343 K⁴⁴). In the vicinity of the glass transition, the fragility is much smaller,²⁹ and a fragile to strong transition might, therefore, be expected.

A second piece of evidence for an anomaly is given by the viscosity behavior using the Speedy-Angell power-law fitting procedure⁷¹ that has been used to analyze the viscosity anomalies occurring in water just before its crystallization,⁹³

$$\eta = A_\eta \left(\frac{T - T_s}{T_s} \right)^{-\gamma_\eta}, \quad (8)$$

where A_η and $\gamma_\eta > 0$ are constants and T_s represents a singular temperature at which η diverges. Just below the melting temperature of GST225 ($T_m = 900$ K), the fit using Eq. (8) of either the τ_α -based viscosity or the experimental data⁶⁹ leads to a strong increase and we find $T_s = 792$ K and $T_s = 707$ K, respectively. The fit on our calculated η (inset of Fig. 9) furthermore leads to $\gamma_\eta = 0.65(3)$ and $A_\eta = 0.050(1)$ mPa s,

whereas for the experimental viscosity data,⁶⁹ one finds $\gamma_\eta = 0.92(6)$ and $A_\eta = 0.603$ mPa s. The same fit applied to the pure tellurium data^{66,70} leads to $T_s = 402$ K and 621 K (see Fig. 5), respectively. While we cannot comment more on the discrepancy between the two sets of experimental data (visible on Fig. 5), we note that the latter fitting parameter T_s (related to the data set of Ref. 70) is nearly identical to the location (623 K) of observed extrema in the specific heat, thermal expansion coefficient, density, compressibility, and related quantities.^{94,95} These anomalies point to a structural phase transition driven by a semiconductor-metal transition close to the melting point, and recent arguments in this direction have been recently reported.³²

Taken together, the present investigation suggests that at some temperature T_s defining the fragile to strong transition, the liquid must undergo some important change in viscosity (Fig. 10), and from the compilation of both sets of data, the jump at $T = T_s$ should lead to a change by at least one order of magnitude in viscosity. Using two VFT forms involving a high temperature fragility ($\mathcal{M}_{HT}$) and a low temperature fragility ($\mathcal{M}_{BT}$) and the fitting parameters determined from the different sets of data, for liquid GST225, we find a jump in viscosity at the transition temperature of $\Delta \log \eta(T_s) = 1.35$. More generally, this jump can be characterized by

$$\Delta \log_{10} \eta(T_s) = 1 + \frac{(\mathcal{M}_{HT} - \mathcal{M}_{BT})(\frac{T_s}{T_g} - 1)}{\mathcal{M}_{BT}(\frac{T_s}{T_g} - 1) + 16} \quad (9)$$

if one assumes $\log \eta_\infty = -4$. The intensity of viscosity change at the fragile to strong transition is, thus, directly linked with the fragility difference between the high- and low-temperature liquids.

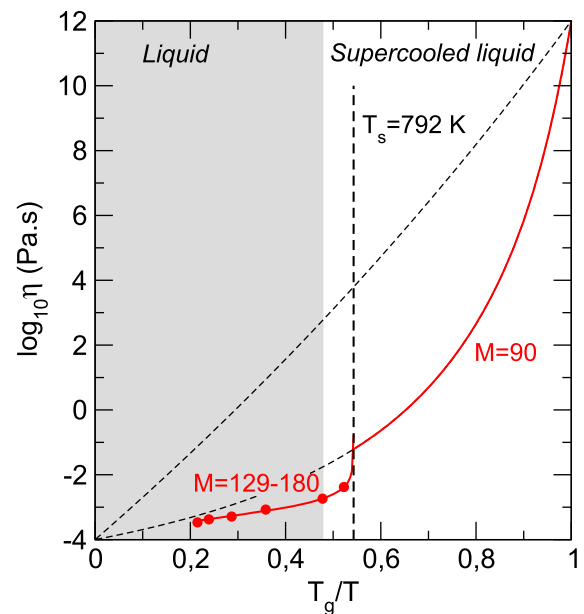


FIG. 10. τ_α calculated viscosities (red circles) represented as a function of T_g/T (here $T_g = 430$ K²⁹). For $T > 792$ K, the solid red line is a Speedy-Angell⁷¹ fit [Eq. (8)] to the data, leading to a singular temperature of 792 K. For $T < T_s$, the red curve represents a VFT curve using the measured fragility $\mathcal{M} = 90$.²⁹ The high temperature fragilities (129-180) result from the VFT fit of the data (see the text for details). The gray zone corresponds to the stable liquid at $T \geq T_m$.

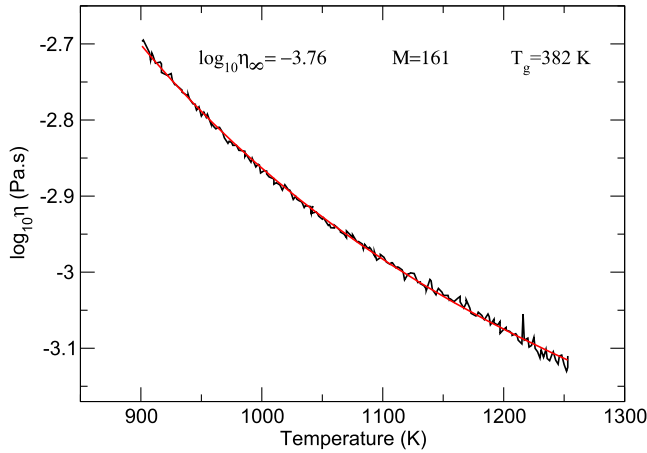


FIG. 11. Measured viscosity of liquid $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ⁶⁹ (black) fitted by a VFT (red) form.

B. High temperature fragility of GST225

Here, we discuss the high temperature fragility determined from recently measured viscosities⁶⁹ of liquid $\text{Ge}_2\text{Sb}_2\text{Te}_5$ using the typical functionals for $\eta(T)$. Indeed, the data have been analyzed only from a simple Arrhenius form in Ref. 69, although the representation (inset of Fig. 9) in an appropriate plot clearly indicates a departure from Arrhenius behavior if the whole temperature range is considered down to T_g . Figure 11 shows the experimental data fitted by the VFT [Eq. (7)]. Three parameters are used for the fit: the viscosity at infinite temperature η_∞ , the liquid fragility $\mathcal{M}$, and the reference glass transition temperature T_g at which η reaches the value of 10^{12} Pa s. The fit leads to $\mathcal{M} = 161$, $T_g = 382$ K, and $\log_{10}\eta_\infty = -3.76$ (correlation coefficient $r = 0.999$). The obtained glass transition temperature T_g is identical to the one determined by Kalb *et al.* ($T_g = 383$ K²⁴) and similar to the value (430 K) determined by Orava *et al.*,²⁹ the fragility index ($\mathcal{M} = 161$) being similar to the one fitted from the τ_α determined viscosities. The present fitted values from experimental data, thus, confirm the rather high fragility of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ liquid in the experimental 900–1300 K temperature range, different from the fragility determined at a low temperature from crystallization kinetics by Orava *et al.*²⁹ ($\mathcal{M} = 90$), as discussed above. It, therefore, also points to a fragile to strong transition.

C. Fragility and phase change melts

The present results and the extremely high fragility of GST225 is a rather interesting feature regarding data storage. In fact, the high fragility of this compound permits one to ensure fast crystallization at high temperatures due to rather low activation barriers for diffusion, of the order of 0.25 eV [Fig. 4(b)] as in other phase change materials (AIST⁹⁶ or Sb_4Te ⁷³). This turns out to be also the case for other typical liquids such as lighter chalcogenides (As_2Se_3 with $E_A = 0.30$ eV¹⁰⁰) or sodium silicates⁹⁸ which do not lead to PC applications. In fact, at high temperatures, all diffusivities are nearly the same for such different systems (Fig. 12). For lower temperatures however, limitations in computational

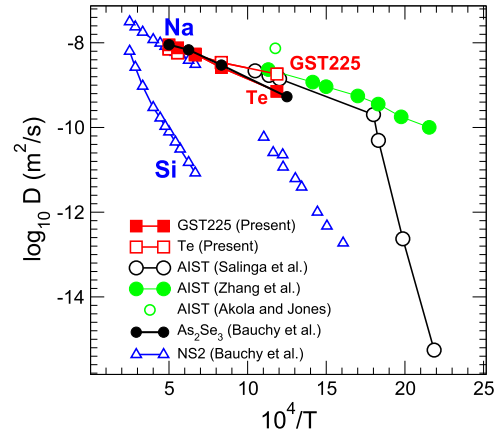


FIG. 12. Calculated and measured diffusion coefficients in different network-forming liquids as a function of inverse temperature: GST225 and Te (present work), AIST [Zhang *et al.* (calculated⁹⁶), Salinga *et al.* (measured³⁰), Akola and Jones (calculated⁹⁷), As_2Se_3 (Bauchy *et al.*¹⁰⁰), and sodium silicate (Bauchy *et al.*, NS2⁹⁸). Note that for the latter, Si and Na species are represented.

power do not allow for a full characterization of the dynamic properties (i.e., close to T_g) and estimates are mostly limited to about $10^4/T \approx 15$. However, a recent experimental investigation³⁰ from crystal growth measurements on AIST permits one to estimate $D(T)$ at low temperatures, and it reveals a dramatic change in behavior (Fig. 12) with activation energies now of the order of 2.78 eV, i.e., lower than the typical activation barrier for recrystallization (3.31 eV in GST225⁹⁹). These large energy barriers are believed to ensure the high stability of the amorphous phase at low temperatures but also indicate a decoupling between viscosity and diffusivity. Notice that the diffusivity data of AIST³⁰ are compatible with the calculated values for diffusion constants at high temperatures.

The growth of this decoupling leads to a well-documented breakdown¹⁰⁰ of the SE relationship [Eq. (3)] that is valid in equilibrated high-temperature liquids. Once the temperature is sufficiently low, the diffusivity becomes, indeed, much higher than its value expected from the viscosity, and such features have been detected from simulations in liquid GeTe. It was shown¹⁰¹ that GeTe has a very high diffusivity (10^{-10} m²/s) down to temperatures close to the glass transition temperature. In addition, dynamic heterogeneities¹⁰² have been evidenced and such inhomogeneous spatial and relaxational fluctuations have been also linked with the breakdown of the SE relation. A correlation between SE deviation and fragility has been proposed,¹⁰³ verified for different glass-forming liquids. Given that GST225 displays an exceptionally large fragility ($\mathcal{M} = 129$ or 161 from experimental data sets⁶⁹), one is led to believe that such a breakdown should occur as well in this prototypal PC material.

V. SUMMARY AND CONCLUSIONS

Here, using MD simulations, we have investigated the dynamic and relaxation properties of liquid $\text{Ge}_x\text{Sb}_x\text{Te}_{100-2x}$ alloys with changing the tellurium content. Previously, we have set extremely accurate structural models with this

DFT-based framework, and corresponding structure functions have been validated by a series of neutron diffraction measurements.¹⁷

Results indicate a global reduction of dynamics at the lowest investigated temperature (820 K) as the Te content decreases, and an Arrhenius behavior is found for the self-diffusion coefficients. These coefficients permit one to evaluate a Stokes-Einstein derived viscosity that is globally compatible with experimental data for liquid Te and GST225. Corresponding activation energies (E_A) show a more stronger dependence of the species and the addition of cross-linking elements (Ge, Sb) leads to a global increase of E_A with only a weak indication of a possible dynamic anomaly for the $\text{Ge}_{10}\text{Sb}_{10}\text{Te}_{80}$ composition.

The investigation of relaxation using the decay of density-density correlations permits one to extract the dependence of the relaxation time $\tau_\alpha(x, T)$ that shows a global increase with increasing (Ge, Sb) content and decreasing temperature. Using such determined values, we calculate a corresponding viscosity that is found to be small and in the domain of fragile liquids. Further analysis suggests that a possible fragile to strong transition can be present in such telluride liquids. In fact, the viscosity behavior at high and low temperatures leads to fragilities that are rather different ($\mathcal{M} = 90$,²⁹ $\mathcal{M} = 129$ from our fitted data, and $\mathcal{M}$ from a VFT fit of experimental data⁶⁹). The large difference in transport behaviour close to the melting point and close to the glass transition is a strong indication for a fragile to strong transition. We identify the corresponding transition temperature at $T_s = 792$ K from a Speedy-Angell fit of our calculated data.

The high fragilities close to the melting temperature for GST225 appear to be a key factor for the phase change data storage. In fact, for $T \leq T_m$, large $\mathcal{M}$ must lead to a dramatic decrease in diffusivity, a property that is suggested to be essential in order to ensure fast crystallization at high temperatures and stable amorphous phases having large energy barriers for diffusion.

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