

Is the λ -transition in liquid sulfur a fragile-to-strong transition?

Cite as: J. Chem. Phys. **151**, 041105 (2019); <https://doi.org/10.1063/1.5110177>

Submitted: 14 May 2019 . Accepted: 03 July 2019 . Published Online: 25 July 2019

Bing Yuan, Bruce Aitken, and Sabyasachi Sen 



View Online



Export Citation



CrossMark

ARTICLES YOU MAY BE INTERESTED IN

Radial distribution functions of water: Models vs experiments

The Journal of Chemical Physics **151**, 044502 (2019); <https://doi.org/10.1063/1.5100871>

Competing chemical and hydrodynamic interactions in autophoretic colloidal suspensions

The Journal of Chemical Physics **151**, 044901 (2019); <https://doi.org/10.1063/1.5090179>

Thermodynamic analysis of the stability of planar interfaces between coexisting phases and its application to supercooled water

The Journal of Chemical Physics **150**, 224503 (2019); <https://doi.org/10.1063/1.5097591>

The Journal
of Chemical Physics

Submit Today

The Emerging Investigators Special Collection and Awards
Recognizing the excellent work of early career researchers!



Is the λ -transition in liquid sulfur a fragile-to-strong transition?

Cite as: J. Chem. Phys. 151, 041105 (2019); doi: 10.1063/1.5110177

Submitted: 14 May 2019 • Accepted: 3 July 2019 •

Published Online: 25 July 2019



View Online



Export Citation



CrossMark

Bing Yuan,¹ Bruce Aitken,² and Sabyasachi Sen^{1,a)} 

AFFILIATIONS

¹Department of Materials Science and Engineering, University of California at Davis, Davis, California 95616, USA

²Science and Technology Division, Corning, Inc., Corning, New York 14831, USA

^{a)}Author to whom correspondence should be addressed: sbsen@ucdavis.edu

ABSTRACT

The abrupt and large increase in the viscosity of liquid sulfur above the λ -transition temperature T_λ corresponds to a reversible structural transformation in the form of a ring-to-chain polymerization reaction. The mechanistic connection between this structural transformation and viscosity is investigated by studying the compositional dependence of the shear relaxation behavior of supercooled $S_x\text{Se}_{100-x}$ liquids as their structural evolution mimics that of liquid sulfur across the λ -transition. The results of steady and oscillatory shear parallel-plate rheometry indicate that the viscosity of these liquids is controlled by the S/Se–S/Se bond scission/renewal dynamics and the time scale of these dynamics rapidly increases as the relative concentrations of rings and chains in the structure become comparable. The coexistence of these two types of topological units in these liquids lowers the conformational entropy of the chain elements due to a steric hindrance from the ring elements, resulting in a rapid drop in the fragility as S is added to Se. The same topological effect resulting from the ring-to-chain transformation in liquid S renders the highly fragile molecular liquid below T_λ , a strong polymerized liquid above T_λ . Therefore, it is argued that the λ -transition of liquid S corresponds to a fragile-to-strong liquid-liquid transition.

Published under license by AIP Publishing. <https://doi.org/10.1063/1.5110177>

The existence and nature of liquid-liquid transitions in glass-forming liquids and their possible continuation into the glassy state are highly debated issues in condensed-matter science.^{1–5} It is reasonable to expect that such a transition would have a signature in the temperature dependence of the shear viscosity η of glass-forming liquids. The functional form of $\eta(T)$ could vary from a nearly-Arrhenius behavior with a single activation energy that is practically independent of temperature, all the way to a strongly non-Arrhenius behavior, where the activation energy increases rapidly with decreasing temperature. Angell has shown that, if η is expressed as a function of T_g/T , i.e., temperature scaled by the glass transition temperature T_g , then a useful classification scheme emerges as a function of the parameter m , which is termed “fragility index” and is defined as⁶

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

The glass-forming liquids with increasingly non-Arrhenius behavior of η are then characterized by progressively increasing values of m . Glass-forming liquids with low and high values of m were

denoted by Angell as “strong” and “fragile,” respectively.⁶ Although m is defined according to Eq. (1) at $T \approx T_g$, the temperature dependence of the viscosity of a glass-forming liquid over the entire range of supercooling can be related to its fragility index. This situation is possibly most directly evident in the MYEGA (Mauro-Yue-Ellison-Gupta-Allan) equation⁷ that describes $\eta(T)$ well for a large variety of glass-forming liquids over a wide range of temperatures and can be written as

$$\log_{10} \eta(T) = \log_{10} \eta_\infty + (\log_{10} \eta_{T_g} - \log_{10} \eta_\infty) \frac{T_g}{T} \times \exp \left[\left(\frac{m}{\log_{10} \eta_{T_g} - \log_{10} \eta_\infty} - 1 \right) \left(\frac{T_g}{T} - 1 \right) \right]. \quad (2)$$

In Eq. (2), $\log_{10} \eta_{T_g}$ and $\log_{10} \eta_\infty$ correspond to the logarithm of shear viscosity at T_g and at infinite temperature, respectively, and the latter quantity is used as a fit parameter in practice. It is clear from Eq. (2) that $\eta(T)$ of a glass-forming liquid over the entire range of supercooling is expected to be characterized by a single value of m . However, a series of studies in recent years on a variety of metallic,

chalcogenide, and halide glass-forming liquids have reported a violation of this behavior, where $\eta(T)$ is characterized by a low value of m , i.e., the liquid is strong at low temperatures near T_g , while the high-temperature viscosity (typically $\eta < 1$ Pa s) is characteristic of that of a fragile liquid with high m .^{8–12} The strength of the fragile-to-strong (FST) has been expressed in terms of the ratio F of the high- and low-temperature fragilities, which typically ranges between $2 \leq F \leq 8$, with metallic liquids being characterized by some of the highest F values.⁸ This FST was hypothesized to signify an underlying liquid-liquid structural transition although the atomistic nature of this transition has remained unclear. Moreover, a recent experimental study has suggested that the existence of the FST, at least in some glass-forming liquids, may be an artifact of the inaccuracies associated with the viscosity measurement technique employed at high temperature and with the derivation of the fragility index from calorimetric methods near T_g .¹²

In contrast with these glass-forming liquids, elemental sulfur presents a unique case of a well-characterized structural transition. Sulfur above its melting point at 119°C is a molecular liquid that predominantly contains S_8 rings and is characterized by viscosities on the order of 10^{-2} Pa s.¹³ The structure of this equilibrium liquid abruptly changes across $T_\lambda \approx 159^\circ\text{C}$, where the rings open up into diradicals and polymerize to form S_n chains.¹⁴ This ring-to-chain transformation, being completely reversible, is an example of “living polymerization” and has been termed in the literature as the λ -transition, as the corresponding jump in the heat capacity C_p shows a cusplike behavior across this transition.¹⁵ Among several other properties that display a sharp change across the λ -transition, the viscosity of liquid sulfur abruptly increases by nearly five orders of magnitude (Fig. 1) from ~ 0.05 Pa s at 160°C to ~ 930 Pa s at 187°C .^{13,16} A further increase in temperature results in a lowering of viscosity (Fig. 1). The thermoreversible nature of the

ring-to-chain transformation process in liquid sulfur and the temperature dependence of the ring:chain ratio above the λ -transition have been studied in detail by Yannopoulos and co-workers using *in situ* high-temperature Raman spectroscopy.¹⁷ Their results indicated a monotonic increase in the S_n polymeric chain fraction in the liquid with increasing temperature at least up to 300°C , although the rate of the ring-to-chain conversion continuously decreases with temperature. Hence, the sudden upward jump in viscosity across T_λ can indeed be ascribed to the polymerization reaction.

However, the determination of the fragility index m of liquid sulfur above and below the λ -transition from relaxation time measurements has been claimed to be problematic in the recent past, due to the presence of multiple relaxation mechanisms and their unknown contributions to viscosity.¹⁴ Directly using the viscosity data for molecular liquid sulfur below the λ -transition¹³ and a glass transition temperature T_g ranging between -23 and -30°C , where the viscosity is $\sim 10^{12}$ Pa s, yields $m \sim 149 \pm 3$ below T_λ (Fig. 1). On the other hand, the viscosity data of the polymerized liquid above T_λ are consistent with those reported^{16,18} for the supercooled liquid obtained from reheating glassy S, quenched from a temperature well above T_λ to preserve the polymeric structure (Fig. 1). When taken together, these viscosity data yield $m \sim 35 \pm 3$ for the polymerized liquid. As such, these results indicate an FST with increasing temperature for liquid sulfur. However, considering the presence of multiple relaxation mechanisms in liquid S, the validity of such a simplistic treatment of the temperature dependence of viscosity remains questionable.

Elemental selenium, as another member of the chalcogen family, shares chemical similarities with sulfur yet exhibits very different properties as a glass-forming liquid. Amorphous selenium and liquid selenium consist practically solely of polymeric Se_n chains and therefore do not display the ring-to-chain transformation that is characteristic of sulfur with increasing temperature.¹⁹ The fragility of selenium is also known to be relatively high with the most reliable estimates of m varying between ~ 70 and 80 .^{20,21}

In a previous Raman and ^{77}Se Nuclear Magnetic Resonance (NMR) study of the S–Se binary system, it was shown that the addition of selenium stabilizes the glassy state and T_g linearly increases with increasing selenium concentration.²² Moreover, both S and Se retain their preferences of forming rings and chains as in their elemental forms, respectively, although heterocyclic $\text{Se}_y\text{S}_{8-y}$ rings ($0 \leq y \leq 8$) and $[\text{S}, \text{Se}]_n$ chains are also formed. Therefore, the S–Se binary liquids display an increasing chain:ring ratio with increasing Se content and thus mimic the topological transformation of molten sulfur above the λ -transition. Here, we report the results of detailed steady and small-amplitude-oscillatory shear (SAOS) rheometric measurements of the viscoelastic relaxation behavior of binary $\text{S}_x\text{Se}_{100-x}$ liquids ($10 \leq x \leq 75$). These results provide important clarification of the atomistic aspects of viscous flow and relaxation in these liquids and confirm that the λ -transition of liquid sulfur indeed corresponds to an FST.

Binary $\text{S}_x\text{Se}_{100-x}$ glasses with $x = 10, 30, 45, 60,$ and 75 were prepared from mixtures of constituent elements (99.999% purity) that were taken in evacuated silica ampoules and melted at 400°C for 24 h. The melts were subsequently quenched by dipping the ampoule in water. Details of the synthesis and thermophysical and

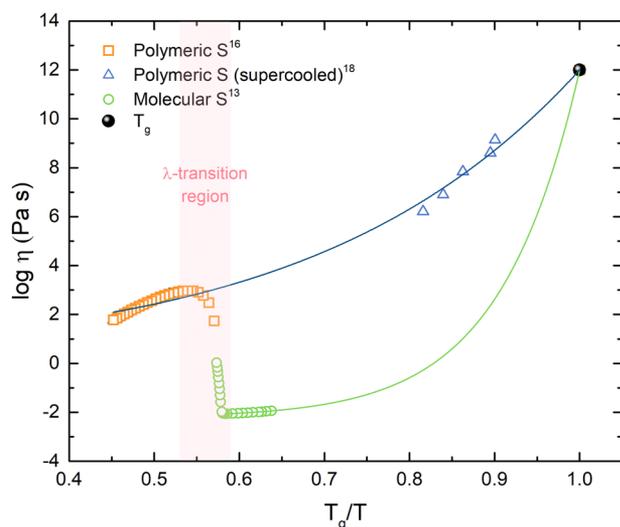


FIG. 1. Viscosity of molecular (circles) and polymeric (squares) liquid sulfur across the λ -transition as a function of T_g/T .^{13,16} Viscosity of polymeric liquid S in its supercooled state is shown with triangles.¹⁸ Viscosity at T_g is taken to be 10^{12} Pa s. Lines through the data are fits of the MYEGA equation.

structural characterization of these glasses are reported in a previous publication.²² The rheological measurements reported in the present study were carried out within the linear viscoelastic regime using an Anton Paar MCR 92 parallel plate rheometer equipped with a Peltier heater, under a constant flow of nitrogen gas. Viscosity measurements on these supercooled S_xSe_{100-x} liquids were carried out under steady shear condition, using a 25 mm diameter upper plate and a stationary lower plate, on samples with a disklike geometry with ~ 0.8 mm thickness. At each temperature, the Newtonian viscosity was measured at several shear rates $\dot{\gamma}$ ranging between 1 s^{-1} and 100 s^{-1} and the average viscosity is reported. The small-amplitude-oscillatory-shear (SAOS) rheometry measurements were carried out using 8 mm diameter plates, and the sample thickness was ~ 1.2 mm. At each temperature, the samples were held for 5 min to attain thermal equilibrium, followed by the application of oscillatory strain with angular frequency ω varying between 0.01 and 600 rad/s, and concomitantly, the torque was measured to obtain the storage and loss moduli G' and G'' as a function of ω .

The shear viscosity of the supercooled S_xSe_{100-x} liquids is shown in Fig. 2 as a function of scaled temperature T_g/T . The fits of the MYEGA equation [Eq. (2)] to these viscosity data are also shown in Fig. 2. The compositional variation of the corresponding m values obtained from these fits is shown in Fig. 3 and compared with the m for Se as reported in the literature^{20,21} and with the above-mentioned m values for molecular and polymerized liquid S. It is clear from Fig. 3 that pure chain and ring environments corresponding to Se and molecular S liquids, respectively, exhibit super-Arrhenius behavior with large m values. On the other hand, the binary S–Se liquids are characterized by lower m , compared to either pure Se or molecular S; m decreases with the initial addition of either S to Se or vice versa, which suggests that the coexistence of chain and ring elements in these liquids results in a rapid decrease in fragility and m reaches a minimum value of ~ 37 in the binary

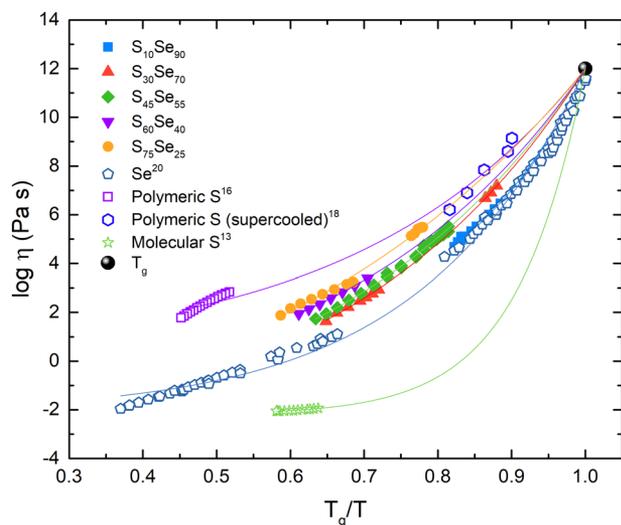


FIG. 2. Viscosity of binary S_xSe_{100-x} liquids measured in the present study. Viscosity data of Se are from Ref. 20 and of S are from Fig. 1. Viscosity at T_g for all compositions is taken to be 10^{12} Pa s. Lines through the data are fits of the MYEGA equation.

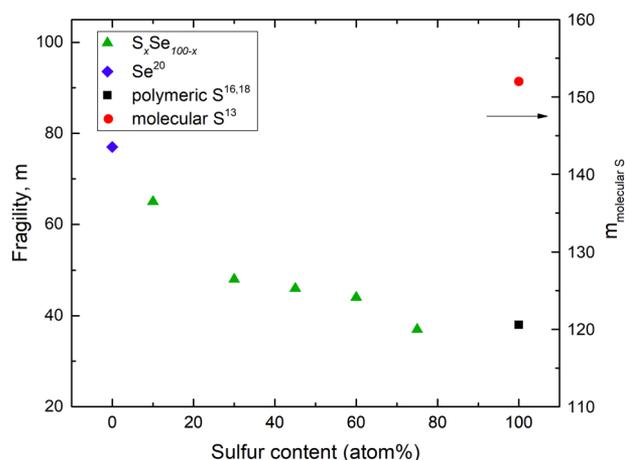


FIG. 3. Compositional dependence of fragility of S_xSe_{100-x} liquids as obtained from the fits of the MYEGA equation in Fig. 2.

$S_{75}Se_{25}$ liquid (Fig. 3). This trend also resembles the variation of m for liquid S itself, which has the highest fragility in the molecular state and the lowest fragility in the polymerized state above the λ -transition (Fig. 3), where the liquid is characterized by the coexistence of comparable fractions of S_8 rings and S_n chains.^{17,23} Sidebottom has pointed out in a series of recent studies the importance of structural connectivity on the fragility of a wide variety of inorganic glass-forming liquids.^{24,25} It may be noted in this regard that the average short-range connectivity of all S_xSe_{100-x} liquids is identical as the coordination number of both S and Se is 2. Therefore, the intermediate-range connectivity and steric effects should be taken into account to explain the remarkable compositional variation of m in these liquids. Further insight into this problem can be obtained from the rheometric measurements of the viscoelastic relaxation processes and time scales in these liquids.

Figure 4 shows the master curves of $G'(\omega)$ and $G''(\omega)$ for the binary S_xSe_{100-x} liquids obtained using time-temperature superposition of the SAOS rheometry data. All master curves display two $G'-G''$ crossovers corresponding to the existence of two separate relaxation processes. Previous studies have reported similar observations on both elemental S and Se liquids; in our earlier rheological investigation of supercooled Se, a slow Debye-like and a fast relaxation process were, respectively, attributed to Se–Se bond scission/renewal dynamics and segmental Se chain motion.²⁶ It is clear from Fig. 4 that the slow relaxation process corresponding to the low-frequency $G'-G''$ crossover is temporally decoupled from the fast process corresponding to the high-frequency $G'-G''$ crossover by several orders of magnitude. The difference $\Delta\tau$ between the fast and the slow relaxation time scales τ_f and τ_s , respectively, increases with increasing sulfur content (Fig. 4). The temperature dependence of τ_f and τ_s for all binary S_xSe_{100-x} liquids is shown in Fig. 5 as a function of T_g/T and is compared with that for supercooled Se. It is evident from Fig. 5 that the time scale and its temperature dependence for the fast process of segmental chain dynamics for all liquids are quite similar. In contrast to τ_f , and similar to viscosity in Fig. 2, τ_s monotonically increases with increasing sulfur content at

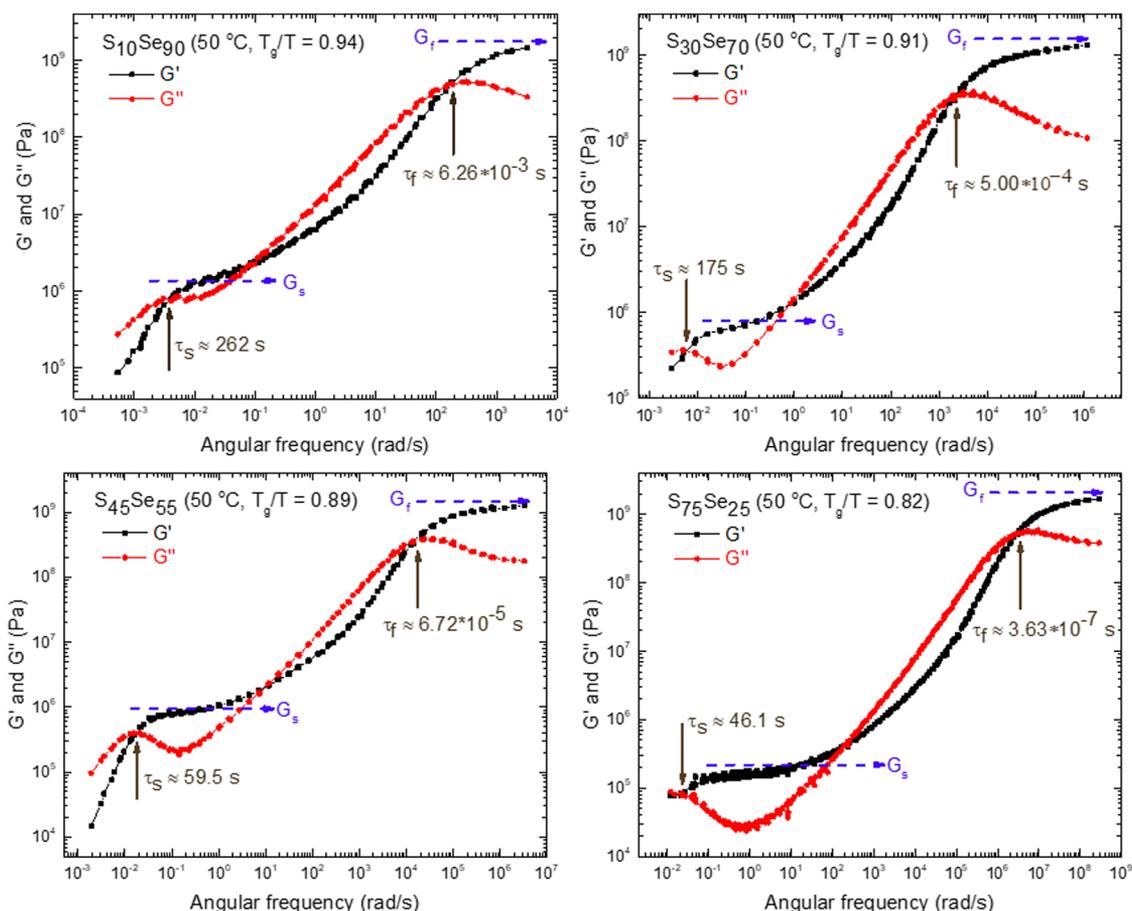


FIG. 4. Master curves of storage modulus G' (squares) and loss modulus G'' (circles) of supercooled binary S_xSe_{100-x} liquids. The TTS reference temperature is listed alongside each composition. Locations of $G'-G''$ crossovers associated with the relaxation times τ_f and τ_s for the fast and slow processes, respectively, are marked by vertical arrows, and the respective values of τ_f and τ_s at the TTS reference temperature are listed alongside. Corresponding shear moduli G_f and G_s are marked by horizontal dashed lines.

identical T_g/T . This behavior is consistent with the observation made in a recent study by Zhu *et al.* that the viscosity of supercooled Se is controlled by the slow process.²⁶ Here, this observation is shown to also hold true for a binary liquid of composition $S_{45}Se_{55}$ (Fig. 6). The relative contribution of the slow and fast processes toward viscosity η can be estimated using the Maxwell equation: $\eta = G\tau$, where τ is the time scale of the process and G is the corresponding shear modulus. The shear moduli G_s and G_f for the fast and slow processes, respectively, can be obtained from the plateau values of $G'(\omega)$ on the high-frequency side of the corresponding $G'-G''$ crossovers in Fig. 4. The viscosity contributions $G_s\tau_s$ and $G_f\tau_f$ from the slow and the fast processes, respectively, are compared to the experimentally measured viscosity in Fig. 6. This comparison immediately indicates that $\eta \approx G_s\tau_s$, while the contribution of $G_f\tau_f$ to viscosity is negligible.

The corresponding activation energies for τ_f and τ_s , respectively, are ~ 230 – 280 kJ/mol and ~ 130 – 170 kJ/mol (Fig. 5). The latter activation energy is indeed similar to the energy required for

S/Se–S/Se bond scission.^{26–28} Assuming that the addition of S to Se should not affect the average chain length in the structure, intuitively one may expect that the fast segmental motion of the chain elements would be relatively unaffected by the appearance of heterocyclic Se_yS_{8-y} rings. This expectation is corroborated by the observation of a weak compositional dependence of τ_f for the S_xSe_{100-x} liquids (Fig. 5). On the other hand, τ_s may increase significantly due to the coexistence of ring and chain elements in the structure, if the latter results in a steric hindrance toward achieving proper orientational configuration of the structural moieties corresponding to the formation of the transition-state activated complexes for the S/Se–S/Se bond scission/renewal process. We hypothesize that this lowering of the chain conformational entropy in the presence of rings is responsible for the lower fragility of the binary S_xSe_{100-x} liquids (Fig. 3). A similar situation is encountered in liquid S (Figs. 1 and 2) as an increasing fraction of the rings open and polymerize into chains with increasing temperature above T_λ . Therefore, the abrupt increase in the viscosity of liquid S across the λ -transition is consistent with

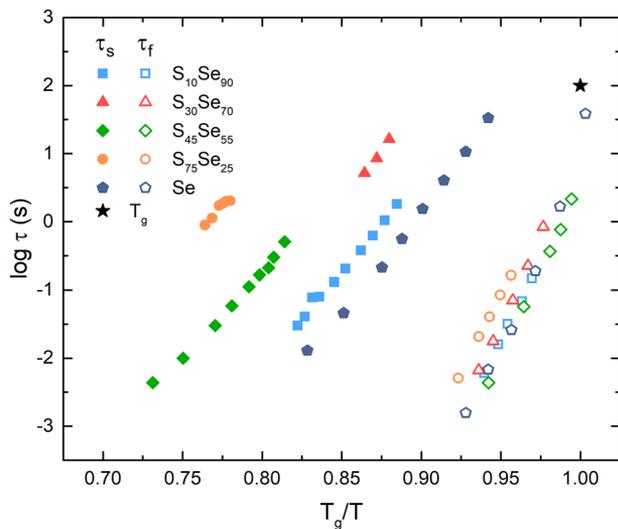


FIG. 5. Temperature dependence of τ_f (open symbols) and τ_s (filled symbols) shown as a function of T_g/T for supercooled binary $S_x\text{Se}_{100-x}$ liquids.

an FST. However, it may be noted here that this transition in liquid S is characterized by a nonmonotonic temperature dependence of viscosity and the fragility of the liquid decreases with increasing temperature across the transition. In contrast, the reported FST in other glass-forming liquids is associated with a monotonic decrease in viscosity and an increase in the fragility across the transition, with increasing temperature.

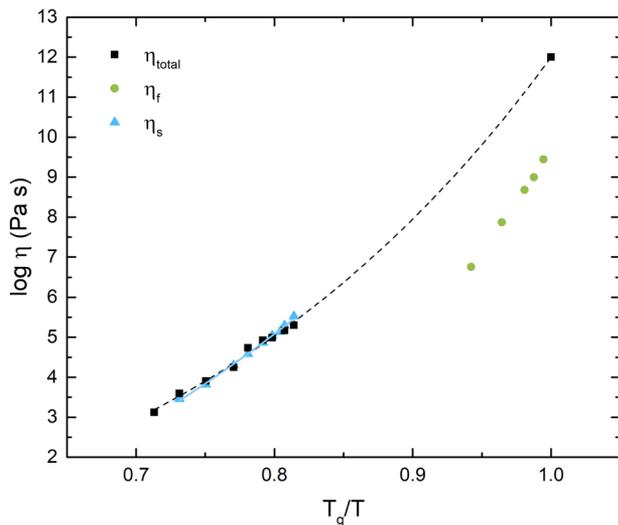


FIG. 6. Viscosity contributions from the slow process $\eta_s = G_s\tau_s$ (triangles) and from the fast process $\eta_f = G_f\tau_f$ (circles) for supercooled $S_{45}\text{Se}_{55}$ liquid. Experimentally measured viscosity (squares) for this liquid and the corresponding MYEGA fit (dashed line) are shown for comparison. Viscosity at T_g is taken to be 10^{12} Pa s.

In summary, the systematic compositional evolution of the viscoelastic relaxation behavior of supercooled $S_x\text{Se}_{100-x}$ liquids indicates that the time scale of the S/Se–S/Se bond scission/renewal dynamics rapidly increases with S concentration as the relative concentrations of rings and chains in the structure become comparable. This observation suggests a lowering of conformational entropy of the chain elements due to a steric hindrance from the ring elements that slows down the orientational rearrangement of structural moieties required for the bond scission/renewal process. This dynamical process, being responsible for viscous flow, renders the $S_x\text{Se}_{100-x}$ liquids progressively less fragile with increasing S concentration. When taken together, these results indicate that the λ -transition in liquid S is also a fragile-to-strong transition.

This work was supported by the National Science Foundation Grant Nos. NSF-DMR 1505185 and NSF-DMR 1855176.

REFERENCES

- P. F. McMillan, M. Wilson, M. C. Wilding, D. Daisenberger, M. Mezouar, and G. Neville Greaves, *J. Phys.: Condens. Matter* **19**, 415101 (2007).
- G. Zhao, Y. J. Yu, and X. M. Tan, *J. Chem. Phys.* **143**, 054508 (2015).
- S. Woutersen, B. Ensing, M. Hilbers, Z. Zhao, and C. Austen Angell, *Science* **359**, 1127 (2018).
- I. Saika-voivod, P. H. Poole, and F. Sciortino, *Nature* **412**, 514 (2001).
- J. H. E. Cartwright, A. G. Checa, J. D. Gale, D. Gebauer, and C. I. Sainz-Díaz, *Angew. Chemie - Int. Ed.* **51**, 11960 (2012).
- C. A. Angell, *J. Non-Cryst. Solids* **131-133**, 13 (1991).
- J. C. Mauro, Y. Yue, A. J. Ellison, P. K. Gupta, and D. C. Allan, *Proc. Natl. Acad. Sci. U. S. A.* **106**, 19780 (2009).
- C. Zhang, L. Hu, Y. Yue, and J. C. Mauro, *J. Chem. Phys.* **133**, 014508 (2010).
- P. Lucas, G. J. Coleman, M. Venkateswara Rao, A. N. Edwards, C. Devaadhithya, S. Wei, A. Q. Alsayoud, B. G. Potter, K. Muralidharan, and P. A. Deymier, *J. Phys. Chem. B* **121**, 11210 (2017).
- J. Orava, H. Weber, I. Kaban, and A. L. Greer, *J. Chem. Phys.* **144**, 194503 (2016).
- S. Stølen, T. Grande, and H. B. Johnsen, *Phys. Chem. Chem. Phys.* **4**, 3396 (2002).
- W. Zhu, M. A. T. Marple, M. J. Lockhart, B. G. Aitken, and S. Sen, *J. Non-Cryst. Solids* **495**, 102 (2018).
- J. Ruiz-García, E. M. Anderson, and S. C. Greer, *J. Phys. Chem.* **93**, 6980 (1989).
- B. Ruta, G. Monaco, V. M. Giordano, F. Scarponi, D. Fioretto, G. Ruocco, K. S. Andrikopoulos, and S. N. Yannopoulos, *J. Phys. Chem. B* **115**, 14052 (2011).
- E. D. West, *J. Am. Chem. Soc.* **81**, 29 (1959).
- G. O. Sofekun, E. Evoy, K. L. Lesage, N. Chou, and R. A. Marriott, *J. Rheol.* **62**, 469 (2018).
- A. G. Kalampounias, K. S. Andrikopoulos, and S. N. Yannopoulos, *J. Chem. Phys.* **118**, 8460 (2003).
- A. Eisenberg and L. A. Teter, *J. Phys. Chem.* **71**, 2332 (1967).
- M. Marple, J. Badger, I. Hung, Z. Gan, K. Kovnir, and S. Sen, *Angew. Chemie* **129**, 9909 (2017).
- P. Košťál and J. Málek, *J. Non-Cryst. Solids* **356**, 2803 (2010).
- P. Košťál and J. Málek, *Pure Appl. Chem.* **87**, 239 (2015).
- B. Yuan, W. Zhu, I. Hung, Z. Gan, B. Aitken, and S. Sen, *J. Phys. Chem. B* **122**, 12219 (2018).
- A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.* **81**, 780 (1959).
- D. L. Sidebottom, *Phys. Rev. E* **92**, 062804 (2015).
- D. L. Sidebottom and S. E. Schnell, *Phys. Rev. B* **87**, 054202 (2013).
- W. Zhu, B. G. Aitken, and S. Sen, *J. Chem. Phys.* **150**, 094502 (2019).
- V. Q. Nguyen, J. S. Sanghera, I. K. Lloyd, I. D. Aggarwal, and D. Gershon, *J. Non-Cryst. Solids* **276**, 151 (2000).
- R. Steudel, *Angew. Chem., Int. Ed. Engl.* **14**, 655 (1975).