Investigation of the Shear Relaxation Behavior of As-Se Liquids Within the Framework of Entropic and Elastic Models of Viscous Flow

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Abstract

The shear relaxation behavior of supercooled arsenic selenide liquids is studied using small amplitude oscillatory parallel plate rheometry. Compositions with >80% Se, characterized by a low-dimensional network of selenium chain segments cross-linked by threefold coordinated arsenic atoms, display the coexistence of a nearly-Arrhenius, slow relaxation process and a strongly non-Arrhenius, fast relaxation process corresponding to bond scission/renewal and chain segmental motion, respectively. The coupling between the weakly non-Arrhenius bond scission and the strongly non-Arrhenius viscosity is achieved near T_g due to the pronounced temperature-dependence of the modulus corresponding to this relaxation process. The temperature dependence of this relaxation modulus is related to the conformational entropy of the chain segments. The large difference between the activation energy of viscous flow and that of the timescale of the relaxation associated with bond scission/renewal implies the need for a revision of the existing models of viscous flow in the literature.

1. Introduction

Viscosity is one of the most important transport properties of glass-forming liquids, both from a fundamental and a technological applications standpoint. Typically the viscosity η of a glass-forming liquid increases by 12 to 15 orders of magnitude upon supercooling, until the glass transition temperature T_g is reached. The activation energy of viscous flow usually increases with the lowering of temperature in a non-Arrhenius manner and η is simply related to the shear relaxation timescale τ through the Maxwell relation $\eta = G_\infty \tau$, where G_∞ is the high-frequency glassy shear modulus. This modulus is considered to be weakly temperature-dependent and is often treated as a constant over the entire temperature range of supercooling such that the entire temperature dependence of η arises from that of τ [1]. The degree of departure of the temperature dependence of viscosity of a supercooled liquid from an Arrhenius behavior is parameterized by its "fragility" index m, which is defined as: $m = \left. \frac{d \log_{10} \eta}{d T_g / T} \right|_{T=T_g}$ [2]. Therefore, higher fragility of a liquid implies stronger departure from Arrhenius behavior.

Several theoretical models have been proposed in the literature to provide a microscopic understanding of the origin of the non-Arrhenius behavior of viscosity of glass-forming liquids, which poses one of the most interesting and challenging problems in the physics of the glass transition. The two most influential models that have gained considerable experimental support are the configurational entropy model and the elastic shoving model. The configurational entropy model was originally proposed by Adam and Gibbs (A-G) in 1965 and was later placed on a more rigorous theoretical footing by Wolynes and coworkers [3,4]. According to the original A-G model, the temperature dependence of the relaxation time τ is proportional to $exp\left(\frac{z\Delta g}{RT}\right)$, where z is the size of a cooperatively rearranging region and Δg is the temperature-independent potential energy barrier associated with the structural rearrangement. Since *z* is believed to increase with decreasing temperature and is inversely proportional to the configurational entropy S_c, the expression for τ can be written as: $\tau = \tau_0\ exp\left(\frac{E}{TS_c}\right)$, where τ_0 is a constant and E is the activation energy of an elementary step in structural relaxation. Since *E* is considered to be independent of temperature, the temperature dependence of τ and, hence, that of η is entirely controlled by that of $S_c(T)$. Rouxel has shown that a temperature-dependent *E* requires the consideration of the temperature dependence of the high-frequency shear modulus $G_\infty(T)$ [1].

On the other hand, a temperature dependent $G_\infty(T)$ is explicitly taken into account in the elastic shoving model proposed by Dyre and coworkers [5–7]. In this model the structural reorganization associated with shear relaxation and viscous flow happens through a local decrease in the density of the surroundings by elastic deformation which creates free volume. Therefore the activation energy for relaxation becomes temperature dependent solely via $G_\infty(T)$ and $\tau = \tau_0 exp\left[\frac{G_\infty(T)V_c}{k_BT}\right]$, where V_c is a temperature-independent characteristic volume of the activated region. Both configurational entropy and elastic shoving models have been successful in predicting the temperature dependence of the experimental viscosity of a wide range of glass-forming liquids from the knowledge of $S_c(T)$ and $G_\infty(T)$ [8–11]. These results, therefore, suggest some deeper physical connection between these two quantities [12,13], although it remains unclear as to which physical picture is correct.

In a recent rheological study of supercooled liquid Se and Se-rich As-Se liquids using small angle oscillatory shear (SAOS), we have demonstrated the existence of two relaxation processes with widely different timescales and relaxation moduli [14]. The slow and fast processes were found to correspond to Se-Se bond breaking/renewal and Se chain segmental motion, respectively

[14,15]. It was shown that the viscosity contribution from the slow process dominates throughout the whole temperature range of supercooled liquid. The contribution from the fast process becomes significant only in the immediate vicinity of T_g, as the glass transition is approached from above. In this study, we extend the previous work to As-Se binary liquids with a wide range of fragility. Results from SAOS rheometry demonstrate the evolution of the two relaxation timescales and their relative contributions to viscosity, as the structure of the liquid evolves with increasing cross-linking and shortening of the selenium chain segments. The relation between the two relaxation timescales and viscosity is examined within the frameworks of the elastic shoving and A-G models.

2. Experimental

2.1 Sample synthesis

The As_xSe_{100-x} ($5\leq x \leq 30$) glasses were synthesized using the conventional melt-quench method. Constituent elements (≥99.999% purity, metal basis) were loaded in an evacuated quartz ampoule, which was subsequently flame sealed and held in a rocking furnace at 650°C for 24 hours. The melts were finally quenched to form glass by dipping the ampoule in cold water.

2.2 Small Amplitude Oscillatory parallel plate rheometry

Two parallel plate rheometers were used in this work: MCR92 (Anton Paar) for compositions with $x\leq 20$, and ARES G2 (TA Instruments) for the $As_{30}Se_{70}$ liquid. The temperature in the MCR 92 rheometer was controlled using a Peltier furnace (up to 200°C), and the upper plate (8 mm diameter) was used to apply strain and measure torque while the bottom plate remained stationary. The temperature in the ARES G2 rheometer was controlled using a forced convection oven (up to 600°C), and the upper and lower plates (both 8 mm in diameter) were used to measure torque and apply strain, respectively. In both setups, the sample was first rapidly heated up to its softening point, and then pressed and trimmed to achieve a sandwich geometry between the two plates with a gap of ~1.5 mm. After reaching thermal equilibrium at each desired measuring temperature, a sinusoidal strain with varying angular frequency ω (600 to 0.01 rad/s) was applied, with its maximum value controlled within a predetermined linear viscoelastic range. Simultaneously the torque was recorded to calculate the storage modulus G′, loss modulus G″ and viscosity η as a function of ω. All measurements were carried out under a constant flow of heated N_2 gas. The temperature range of the experiments was chosen to cover from ~0.8 to 1 on a T_g/T scale.

It may be noted that systematic error in the modulus could be introduced during the measurement of the high-frequency mechanical response of a relatively stiff material such as inorganic glass-forming liquids using rotational rheometers if the role of instrument compliance is not taken into account[16]. The magnitude of such errors has been estimated using the relation $\frac{1}{K_m^*} = \frac{1}{K_s^*} + \frac{1}{K_i^*}$ for the instrument compliance correction [16]. In this relation the parameters K_m^*, K_s^* and K_i^* correspond to the measured, true (sample) and instrument complex torsional stiffness values. The relation between sample torsional stiffness and sample shear modulus is given by: $K = \pi G R^4/2h$, where R is the plate radius (4 mm) and h is the sample thickness (~1.5 mm). The instrument can be approximated as an ideal elastic solid and therefore K_i^* is treated as a real number. The sample storage and loss moduli can then be calculated from the above relation. All rheometry data collected in this study were corrected following this protocol using an instrument compliance of $1/K_i^* = 1.625\text{x}10^{-3}$ rad/Nm [17] obtained from the system calibration.

2.3 Creep recovery experiment

The creep recovery experiments were conducted on the MCR92 (Anton Paar) parallel plate rheometer at various temperatures above T_g. After trimming the sample to the same sandwich geometry as in the oscillatory rheometry, a constant stress was applied to the sample while the strain was recorded as a function of time. After reaching steady state where the strain rate no longer changes with time, the stress was released and the strain relaxation was recorded until equilibrium. The strain in the recovery phase was fitted to the well-known expression:

$$\epsilon(t) = \sigma J(t) = \sigma \left[J_{max} - J_0 - \sum_{i=1}^{3} J_{mi} \left(1 - exp\left(-\frac{t-t_0}{\tau_i} \right) \right) \right] \tag{1}$$

where σ is the stress in the loading phase, J_{max} is the highest compliance reached, J_0 is the glassy compliance, t_0 is the time when stress load was released. The steady state recoverable compliance is given by the expression: $J_{e0} = J_0 + \sum_{i=1}^{3} J_{mi}$.

3. Results and Discussion

The temperature-dependent G′ and G″ spectra of select As_xSe_{100-x} compositions are shown in Fig. 1. At each temperature, the whole spectrum is only partially revealed in the fixed observation window. With increasing temperature, the spectrum gradually shifts from low to high frequency, which enables a sequential observation of a wide frequency range. It has been shown in a previous study that time-temperature superposition (TTS) is not strictly obeyed by these liquids[18]. However, here we have approximated TTS solely for the convenience of visualization of the data over the entire frequency range, and the corresponding “approximate” master curves for G′ and G″ generated through TTS are shown in Fig. 1. It is well-known that for a simple viscoelastic system, such as a Maxwell element consisting of a spring and a dashpot in series, the relaxation frequency corresponds to where G′ = G″, i.e. at the G′-G″ crossover[19]. For all compositions, a G′-G″ crossover can be clearly observed at low temperatures such that at frequencies above this crossover G′ gradually reaches a plateau that is on the order of ~1 GPa. This plateau represents the high-frequency shear modulus G_∞, which for As-Se glasses with ≤30% As varies within the range of ~ 3-6 GPa at ambient temperature [20]. Moreover, for compositions with ≥ 20% As, G′ and G″ immediately decrease with decreasing frequency below the crossover following a slope of 2 and 1, respectively. These two slopes agree with the prediction of the Maxwell model in the low frequency limit, which signifies that below the G′-G″ crossover supercooled liquids with ≥ 20% As enter the terminal regime where the structure is fully relaxed. Identification of the inverse of the crossover frequency as the average shear relaxation timescale τ allows for the estimation of shear viscosity η of these liquids from the Maxwell relation $\eta = G_\infty \tau$. These estimates obtained using a constant value of G_∞ obtained from Fig. 1 for all liquids, are compared with the measured viscosity in Fig. 2. The fragility indices obtained from fitting the MYEGA function [21] to the experimental and the estimated viscosity data are listed in Table 1. Although G_∞ is expected to gradually decrease with temperature above T_g, the effect on viscosity, expressed on a logarithmic scale, of such a drop would be negligible and viscosity will be dominated by the temperature dependence of τ.

It is clear from Fig. 2 that the estimated viscosity values agree rather well with experiment for liquids with ≥ 15% As. However, for liquids with ⩽ 10% As, the viscosity is significantly underestimated, and its activation energy is overestimated as the temperature increases beyond T_g. Clearly, this discrepancy in the activation energies will only worsen if a temperature dependent decrease of G_∞ is incorporated in the Maxwell relation for the estimation of viscosity. A similar observation was reported in a recent study on supercooled Se liquid [14]. An answer to this apparently puzzling behavior can be sought in Fig. 1 where, for compositions with ≤ 10% As, a second G′-G″ crossover can be observed before the terminal regime is reached at lower frequencies. The appearance of this second crossover is a clear indication of the existence of a slower relaxation process, similar to that observed in polymers with strong intermolecular interactions such as chain entanglement or hydrogen bonding [19,22–24]. It is also clear from Fig. 1 that this relaxation is characterized by a modulus that is significantly softer than G_∞ in the temperature range of these measurements. Therefore, similar to G_∞, another shear relaxation modulus can be defined for the slow process. For the sake of clarity in the following discussion, the two shear relaxation moduli that correspond to the slow and fast process are denoted G_s and G_f and the corresponding relaxation timescales are denoted τ_s and τ_f, respectively.

The temperature dependence of the two relaxation timescales τ_s and τ_f for liquids with ≤ 15% As is shown in Fig. 3. It can be seen that, compared to τ_s which is relatively Arrhenius, τ_f has a stronger temperature dependence of the activation energy i.e. the latter is significantly more non-Arrhenius. This difference can be seen more clearly from Table 2 where the fragility indices obtained from MYEGA fittings for both relaxation times are demonstrated. Increasing the As content results in a nearly parallel shift of τ_s towards shorter times and lower temperatures, while maintaining a relatively constant activation energy of around 170 kJ/mol for the different compositions. The relatively constant activation energy of τ_s across all compositions matches with the bond energy of Se-Se and As-Se bonds [25]. On the other hand, τ_f reaches ~ 100s for all liquids near the calorimetric glass transition (Fig. 3). More interestingly, τ_f *vs*. T_g/T remains practically unchanged until the As content exceeds 10%, from where τ_f gradually shifts towards τ_s. Eventually the fast dynamical process disappears at higher As content (≥ 20% As), where the

Se chain segments become non-existent or too short to sustain any segmental motion. At this point only one relaxation time can be identified (Fig. 3).

In our previous work on supercooled Se liquid, the slow and fast relaxation processes were tentatively assigned to Se-Se bond scission/renewal and Se chain segmental motion, respectively, based on their activation energy and the distribution of relaxation times [14]. A recent high-temperature ^{77}Se nuclear magnetic resonance (NMR) spectroscopic study has identified the bond scission/renewal and Se chain segmental dynamics and the associated timescales in supercooled $As_{10}Se_{90}$ liquid [15]. These timescales are shown in Fig. 4 to be in good agreement with the present rheological measurements of τ_s and τ_f, which provides direct validation of the structural assignment of the slow and fast processes in these Se-rich liquids.

In the case of the Se-rich liquids with ≤ 15% As, the presence of two different relaxation processes with significantly different relaxation times and the corresponding relaxation moduli warrant the use of a modified Maxwell relation to obtain viscosity[26–28], where:

$$\eta(T) = G_s\tau_s(T) + \left(G_f - G_s\right)\tau_f(T) \qquad (2)$$

As was shown by Levesque et al.[26], this expression can be derived upon consideration of the equality between the bulk viscosity η of a liquid and the Fourier-Laplace transform of the transverse current correlation function $C_t(Q,t)$ at small times (infinite frequency) and in the hydrodynamic limit of the wavevector Q approaching zero. At this limit, the Fourier-Laplace transform of $C_t(Q,t)$ yields the standard Maxwell relation $\eta = G_\infty\tau$ if the liquid is characterized by a single relaxation time. However, in the presence of two processes with significantly different relaxation timescales, $C_t(Q,t)$ becomes the sum of two contributions, which yields Eqn. 2 [26]. In this expression the first and the second terms represent approximately the viscosity contributions from the slow and the fast process, respectively. The temperature dependence of viscosity in Eqn. 2 originates entirely from that of the relaxation timescales, while the shear moduli are treated to a first approximation as temperature-independent constants, as they do not show significant temperature dependence within the observation window in the spectra in Fig. 1. While this approximation holds well for G_f near T_g, a previous study by Faivre and Gardissat reported a large temperature dependence of G_s for supercooled Se, where the latter was found to drop by nearly three orders of magnitude with increasing temperature from $T_g/T \sim 1.0$ to ~ 0.9, before reaching a plateau [29]. Moreover, in a study of the rheological behavior of Se, Plazek related the onset of the slow process in the G′ spectrum to the steady state recoverable creep compliance J_{e0}, which can be used to estimate the value of $G_s = 1/ J_{e0}$ [22].

The J_{e0} values of $As_{10}Se_{90}$ and $As_{15}Se_{85}$ obtained from creep recovery measurements carried out in the present study at various temperatures near and above T_g are plotted in Fig. 5 (a), together with the data from a previous study by Bernatz et al. for a range of As_xSe_{100-x} compositions [30]. It is clear from Fig. 5a that, for the high Se-containing compositions, there is a large increase in J_{e0} (or a decrease in G_s) within a narrow temperature range of 10-20 K above T_g. J_{e0} reaches a plateau with further increase in temperature and remains constant, which agrees with the observation of a constant G_s from the rheological spectra in Fig. 1 in the same temperature range. The extent of the rise in J_{e0} in the vicinity of T_g decreases with increasing amount of As in the system such that at $x \geq 20$ almost no change in J_{e0} could be observed. From the temperature dependent behavior of J_{e0} it can be concluded that, for compositions with multiple relaxation processes, G_s experiences a significant increase as temperature is lowered to within 15K above T_g (Fig. 5b). Therefore, Eqn. 2 needs to be modified such that:

$$\eta(T) = G_s(T)\tau_s(T) + \left(G_f - G_s(T)\right)\tau_f(T) \tag{3}$$

The viscosity of the Se-rich compositions with ≤ 15% As are then calculated using Eqn. 3 along with the τ_s and τ_f values obtained from rheometry (Fig. 6). It is intriguing to see that viscosities calculated using the modified Maxwell relation reproduce the experimental data rather well, over six orders of magnitude variation in viscosity. The viscosity contributions from the slow process (first term in Eqn. 3) and the fast process (second term in Eqn. 3), as shown in Fig. 6, clearly indicate that the bond breaking/renewal process is the major contributor to viscous flow over the entire temperature/viscosity range. However, the strong temperature dependence of G_s in Eqn. 3 (Fig. 5) also implies that the temperature dependence of the activation energy $E_\tau(T)$ of τ_s is rather different from that of viscosity $E_\eta(T)$ in the immediate vicinity of the glass transition. The coupling of the slow process to viscosity is governed by the temperature dependence of $G_s(T)$ at T ~ T_g and the variation of $E_\eta(T)$ results practically entirely from $G_s(T)$. This observation can only be made consistent with the elastic model of Dyre and coworkers if $E_\tau(T)$ is related to the temperature dependence of the high-frequency elastic modulus $G_f(T)$, and $G_s(T)$ only appears in the Maxwell relation linking the viscosity and relaxation time as in Eqn. 3 such that $\eta = G_s(T) * \left[\tau_0 exp\left(G_f(T)V_c/k_BT\right)\right]$. It was shown in a previous study of the rheological behavior of supercooled Se that bond scission/renewal is a Debye-like process with a nearly-Arrhenius temperature dependence and, therefore, represents non-cooperative isolated events in the structure [14]. However, the local displacement of the surrounding atoms that needs to happen as a precursor of bond-breaking/renewal would likely ensure that the activation energy of τ_s is controlled by $G_f(T)$, as suggested in the elastic model. In contrast with the elastic model, the A-G model assigns the temperature dependence of $E_\tau(T)$ completely to $S_c(T)$ and it is clear from Fig.

3 that the difference in $E_\tau(T)$ between the different compositions in this temperature range is too small to explain the rather large difference in fragility between pure Se (m ~80) and $As_{15}Se_{85}$ (m ~35) solely on the basis of the variation in $S_c(T)$.

It is reasonable to speculate that the two relaxation processes in liquids with ≤15% As may be interconnected. The physical picture behind this hypothesis is that every bond scission or renewal event requires the realization of specific local atomic configurations which can be facilitated through chain segmental motion. However, the mechanism of coupling of the two processes with viscous flow is quite different at $T \sim T_g$. The chain segmental motion is characterized by a strongly temperature dependent timescale $\tau_f(T)$, which is consistent with the expectation that such a dynamical process would involve cooperative displacement of a large number of atoms. The size of these cooperatively rearranging regions likely increases with decreasing temperature, while the corresponding elastic modulus does not change appreciably with temperature. Thus, the coupling between chain motion and viscous flow is consistent with the predictions of both elastic and entropic models. Nevertheless, this process decouples from viscous flow almost immediately above T_g (Fig. 2). On the other hand, the bond scission/renewal dynamics couple with viscous flow over the entire temperature range but yield the correct fragility at $T \sim T_g$ only via the strongly temperature dependent relaxation modulus $G_s(T)$.

The shear modulus of a supercooled liquid can have contributions from both solid-like uniform (affine) deformation as well as the liquid-like (non-affine) local atomic rearrangement due to relaxation, the latter being strongly temperature dependent and unique to amorphous materials [12,13,31]. The latter contribution from the local atomic rearrangement has been shown to be always negative, which softens the shear modulus, and is responsible for the significantly lower shear modulus of a glass compared to its crystalline counterpart. In glass-forming liquids with structural units such as chains and rings, substantial cooperative structural rearrangement via fast chain and ring motion can take place in between low-frequency bond breaking events. As a result, the two relaxation processes give rise to a two-step decrease in the modulus in Se-rich liquids with relatively long Se chain segments (Fig. 1).

From a compliance perspective, the change in J_{e0} is a measure of the configurational entropy difference between a fully relaxed amorphous chain structure and a structure of well stretched/aligned chains under a steady state shear flow [22]. Therefore, G_s is closely related to the available configurational entropy in the system without accessing the configurational states that require bond scission/renewal. This entropy is then precisely the chain conformation entropy which is a sensitive function of the length of the selenium chain segments in the structure. In fact, recent studies have shown that the compositional variation of this conformational entropy closely follows the corresponding variation in the fragility of the supercooled liquids in the As-Se and Ge-Se systems [32]. However, as noted above, the difference between $E_\tau(T)$ and $E_\eta(T)$ in Figs. 2 and 6 implies that this conformational entropy is not the same as the configurational entropy in the A-G model in the sense that the former does not influence the activation energy of τ but affects that of η as a temperature dependent multiplier of τ_s in the Maxwell expression. Therefore, when taken together, the results presented in this work suggest that modifications are necessary to both elastic and entropic models of viscous flow in order to take into account the roles of multiple dynamical processes in the shear relaxation of complex glass-forming chalcogenide liquids characterized by the coexistence of widely different structural elements.

4. Conclusions

Arsenic selenide liquids with < 20 atom% As are characterized by weakly non-Arrhenius, slow bond scission/renewal dynamics and strongly non-Arrhenius, fast chain segmental dynamics. The shear modulus G_f associated with the chain motion corresponds to the traditional glassy modulus G_∞ and does not display significant temperature dependence. On the other hand, the shear modulus G_s corresponding to bond scission dynamics is highly temperature dependent – rising up to 3 orders of magnitude with lowering of temperature, within 20 K above T_g. For Se-rich samples, where two relaxation processes coexist, the viscosity contribution from the fast chain dynamics is negligible except in the immediate vicinity of T_g. On the other hand, the contribution from the slow bond scission process is found to control viscous flow over the entire temperature range. The coupling between the strongly non-Arrhenius viscosity and the nearly-Arrhenius bond scission dynamics near T_g is achieved solely via the strong temperature dependence of G_s, which is related to the conformational entropy of the selenium chain segments. This conformational entropy is eventually lost due to the shortening of the selenium chain length at higher As content. As a result, liquids with 20% As behave as typical network liquids with a single characteristic shear relaxation timescale and its product with the corresponding temperature-independent glassy modulus, following the Maxwell relation, yields viscosity values consistent with experiments. The large difference in the temperature dependence of the activation energy of viscous flow and that of the corresponding slow relaxation timescale in Se-rich liquids with low-dimensional networks is unprecedented in glass-forming liquids to date and warrants some revision of the existing models of viscous flow.

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References

[1] T. Rouxel, Thermodynamics of viscous flow and elasticity of glass forming liquids in the glass transition range, J. Chem. Phys. 135 (2011) 184501.

[2] C.A. Angell, Relaxation in liquids, polymers and plastic crystals—strong/fragile patterns and problems, J. Non. Cryst. Solids. 131 (1991) 13–31.

[3] G. Adam, J.H. Gibbs, On the temperature dependence of cooperative relaxation properties in glass-forming liquids, J. Chem. Phys. 43 (1965) 139–146.

[4] X. Xia, P.G. Wolynes, Fragilities of liquids predicted from the random first order transition theory of glasses., Proc. Natl. Acad. Sci. U. S. A. 97 (2000) 2990–4. doi:10.1073/pnas.97.7.2990.

[5] J.C. Dyre, N.B. Olsen, T. Christensen, Local elastic expansion model for viscous-flow activation energies of glass-forming molecular liquids, Phys. Rev. B. 53 (1996) 2171–2174. doi:10.1103/PhysRevB.53.2171.

[6] J.C. Dyre, Colloquium: The glass transition and elastic models of glass-forming liquids, Rev. Mod. Phys. 78 (2006) 953.

[7] J.C. Dyre, T. Christensen, N.B. Olsen, Elastic models for the non-Arrhenius viscosity of glass-forming liquids, J. Non. Cryst. Solids. 352 (2006) 4635–4642.

[8] P. Richet, Residual and configurational entropy: Quantitative checks through applications of Adam–Gibbs theory to the viscosity of silicate melts, J. Non. Cryst. Solids. 355 (2009) 628–635. doi:10.1016/J.JNONCRYSOL.2009.01.027.

[9] B. Xu, G.B. McKenna, Evaluation of the Dyre shoving model using dynamic data near the glass temperature, J. Chem. Phys. 134 (2011) 124902.

[10] J.C. Dyre, W.H. Wang, The instantaneous shear modulus in the shoving model, J. Chem. Phys. 136 (2012) 224108. doi:10.1063/1.4724102.

[11] L. Larini, A. Ottochian, C. De Michele, D. Leporini, Universal scaling between structural relaxation and vibrational dynamics in glass-forming liquids and polymers, Nat. Phys. 4 (2008) 42–45. doi:10.1038/nphys788.

[12] Y.Q. Cheng, E. Ma, Intrinsic shear strength of metallic glass, Acta Mater. 59 (2011) 1800–1807. doi:10.1016/J.ACTAMAT.2010.11.046.

[13] S. Sen, Entropic vs. elastic models of fragility of glass-forming liquids: Two sides of the same coin?, J. Chem. Phys. 137 (2012) 164505. doi:10.1063/1.4759155.

[14] W. Zhu, B.G. Aitken, S. Sen, Observation of a dynamical crossover in the shear relaxation processes in supercooled selenium near the glass transition, J. Chem. Phys. 150 (2019) 94502.

[15] W. Zhu, I. Hung, Z. Gan, B. Aitken, S. Sen, Dynamical Processes related to viscous flow in a supercooled arsenic selenide glass-forming liquid: Results from high-temperature ^{77}Se NMR Spectroscopy, J. Non. Cryst. Solids. (2019).

[16] S.A. Hutcheson, G.B. McKenna, The measurement of mechanical properties of glycerol, m-toluidine, and sucrose benzoate under consideration of corrected rheometer compliance: An in-depth study and review, J. Chem. Phys. 129 (2008) 74502.

[17] S. Sen, W. Zhu, B.G. Aitken, Behavior of a supercooled chalcogenide liquid in the non-Newtonian regime under steady vs. oscillatory shear, J. Chem. Phys. 147 (2017) 034503.

[18] W. Zhu, B.G. Aitken, S. Sen, Communication: Observation of ultra-slow relaxation in supercooled selenium and related glass-forming liquids, J. Chem. Phys. 148 (2018). doi:10.1063/1.5022787.

[19] J.D. Ferry, Viscoelastic properties of polymers, John Wiley & Sons, 1980.
[20] Y. Gueguen, T. Rouxel, P. Gadaud, C. Bernard, V. Keryvin, J.-C. Sangleboeuf, High-temperature elasticity and viscosity of Ge_xSe_{1-x} glasses in the transition range, Phys. Rev. B. 84 (2011) 64201.
[21] J.C. Mauro, Y. Yue, A.J. Ellison, P.K. Gupta, D.C. Allan, Viscosity of glass-forming liquids, Proc. Natl. Acad. Sci. 106 (2009) 19780–19784.
[22] D.J. Plazek, I. Echeverría, Don't cry for me Charlie Brown, or with compliance comes comprehension, J. Rheol. 44 (2000) 831–841.
[23] C. Gainaru, R. Figuli, T. Hecksher, B. Jakobsen, J.C. Dyre, M. Wilhelm, R. Böhmer, Shear-modulus investigations of monohydroxy alcohols: evidence for a short-chain-polymer rheological response, Phys. Rev. Lett. 112 (2014) 98301.
[24] A. Schönhals, E. Schlosser, Relationship between segmental and chain dynamics in polymer melts as studied by dielectric spectroscopy, Phys. Scr. 1993 (1993) 233.
[25] T.L. Cottrell, The strengths of chemical bonds, Academic Press, 1958.
[26] T. Scopigno, S.N. Yannopoulos, F. Scarponi, K.S. Andrikopoulos, D. Fioretto, G. Ruocco, Origin of the λ Transition in Liquid Sulfur, Phys. Rev. Lett. 99 (2007) 25701.
[27] J.P. Boon, S. Yip, Molecular hydrodynamics, Courier Corporation, 1991.
[28] D. Levesque, L. Verlet, J. Kürkijarvi, Computer "experiments" on classical fluids. IV. Transport properties and time-correlation functions of the Lennard-Jones liquid near its triple point, Phys. Rev. A. 7 (1973) 1690–1700. doi:10.1103/PhysRevA.7.1690.
[29] G. Faivre, J.L. Gardissat, Viscoelastic properties and molecular structure of amorphous selenium, Macromolecules. 19 (1986) 1988–1996.
[30] K.M. Bernatz, I. Echeverría, S.L. Simon, D.J. Plazek, Characterization of the molecular structure of amorphous selenium using recoverable creep compliance measurements, J. Non. Cryst. Solids. 307 (2002) 790–801.
[31] L.S. Huo, J.F. Zeng, W.H. Wang, C.T. Liu, Y. Yang, The dependence of shear modulus on dynamic relaxation and evolution of local structural heterogeneity in a metallic glass, Acta Mater. 61 (2013) 4329–4338. doi:10.1016/J.ACTAMAT.2013.04.004.
[32] S. Sen, Y. Xia, W. Zhu, M. Lockhart, B. Aitken, Nature of the floppy-to-rigid transition in chalcogenide glass-forming liquids, J. Chem. Phys. 150 (2019) 144509. doi:10.1063/1.5092841.
[33] P. Koštál, J. Málek, Viscosity of selenium melt, J. Non. Cryst. Solids. 356 (2010) 2803–2806.
[34] J.D. Musgraves, P. Wachtel, S. Novak, J. Wilkinson, K. Richardson, Composition dependence of the viscosity and other physical properties in the arsenic selenide glass system, J. Appl. Phys. 110 (2011) 063503/1–6. doi:10.1063/1.3638122.

Table 1

Fragility index obtained from MYEGA fitting of literature viscosity data and τG_∞ in Fig. 2.

Composition	Literature	τG_∞
Se	70±3	80±9
As_5Se_{95}	58±4	92±9
$As_{10}Se_{90}$	55±2	70±4
$As_{15}Se_{85}$	45±2	44±5
$As_{20}Se_{80}$	40±4	43±6
$As_{30}Se_{70}$	33±1	35±1

Table 2

Fragility index obtained from MYEGA fitting of the relaxation times of slow (τ_s) and fast (τ_f) processes in Fig. 3.

Composition	τ_s	τ_f
Se	43±3	77±7
As5Se95	35±2	91±7
As10Se90	27±5	70±5
As15Se95	27±4	44±5
As20Se80	44±8	Not present
As30Se70	40±2	Not present

Figure Captions

Figure 1. Frequency dependence of G′ (solid line) and G″ (dashed line) at select temperatures for As_5Se_{95}, $As_{10}Se_{90}$, $As_{20}Se_{80}$ and $As_{30}Se_{70}$ liquids. Approximate master curves generated through TTS, for each composition, are shown in the right column. Corresponding reference temperature for each master curve is shown in the inset.

Figure 2. τG_∞ (blue open symbols) as a function of T_g/T obtained from rheometry are compared with viscosity values (solid symbols or solid lines) from literature [30,33,34]. Dashed blue line through the data are fits of the Tamman-Vogel-Fulcher (TVF) equation to the τG_∞ data.

Figure 3. τ_s (filled symbols) and τ_f (open symbols) as a function of T_g/T for liquids with two relaxation processes. Solid lines and dashed lines are the TVF fits to the data. The single relaxation timescale for $As_{20}Se_{80}$ and $As_{30}Se_{70}$ liquids are shown as blue diamonds and triangles, respectively. Dotted and dashed-dotted lines through these data are the corresponding TVF fits.

Figure 4. Dynamical timescales for $As_{10}Se_{90}$ liquid, obtained from rheological measurements (filled symbols) and ^{77}Se NMR measurements (open symbols), respectively, as a function of T_g/T. NMR timescales are from (*15*).

Figure 5. (a) Steady state recoverable compliance J_{e0} for all compositions plotted against $T-T_g$. Compositions are listed alongside each data set. Dashed lines are guides to the eye. (b) $G_s = 1/J_{e0}$ as a function of T_g/T. Shaded area demonstrates the approximate values of G_∞. Dashed lines are drawn to guide reader's eyes.

Figure 6. Total viscosity (open squares) and the contributions from slow (open circles) and fast processes (open triangles) calculated from the modified Maxwell relation of Eqn. 3. The lines

through these data are TVF fits. Solid symbols and solid lines are viscosity data from literature [30,33,34].

Figure 1

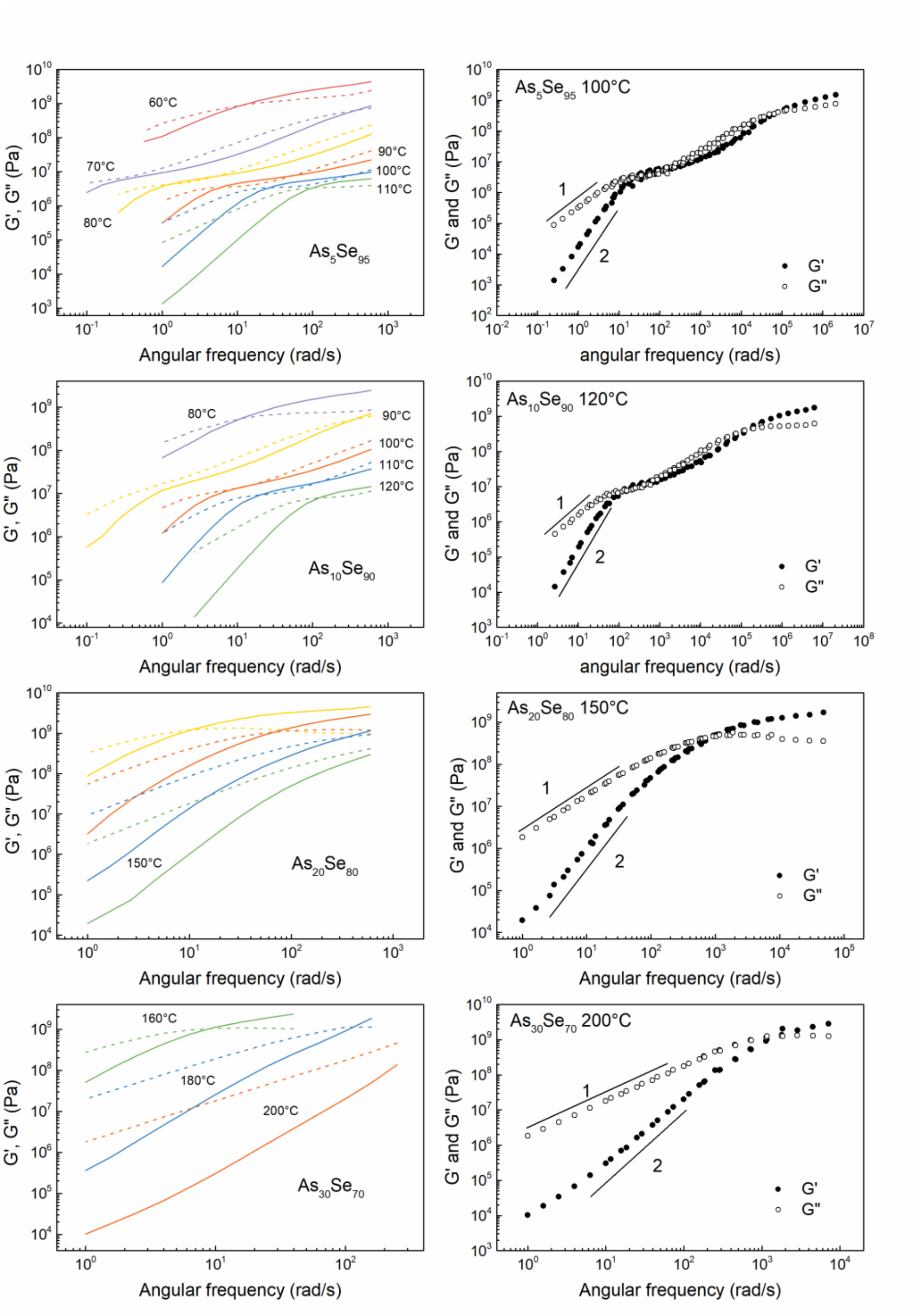
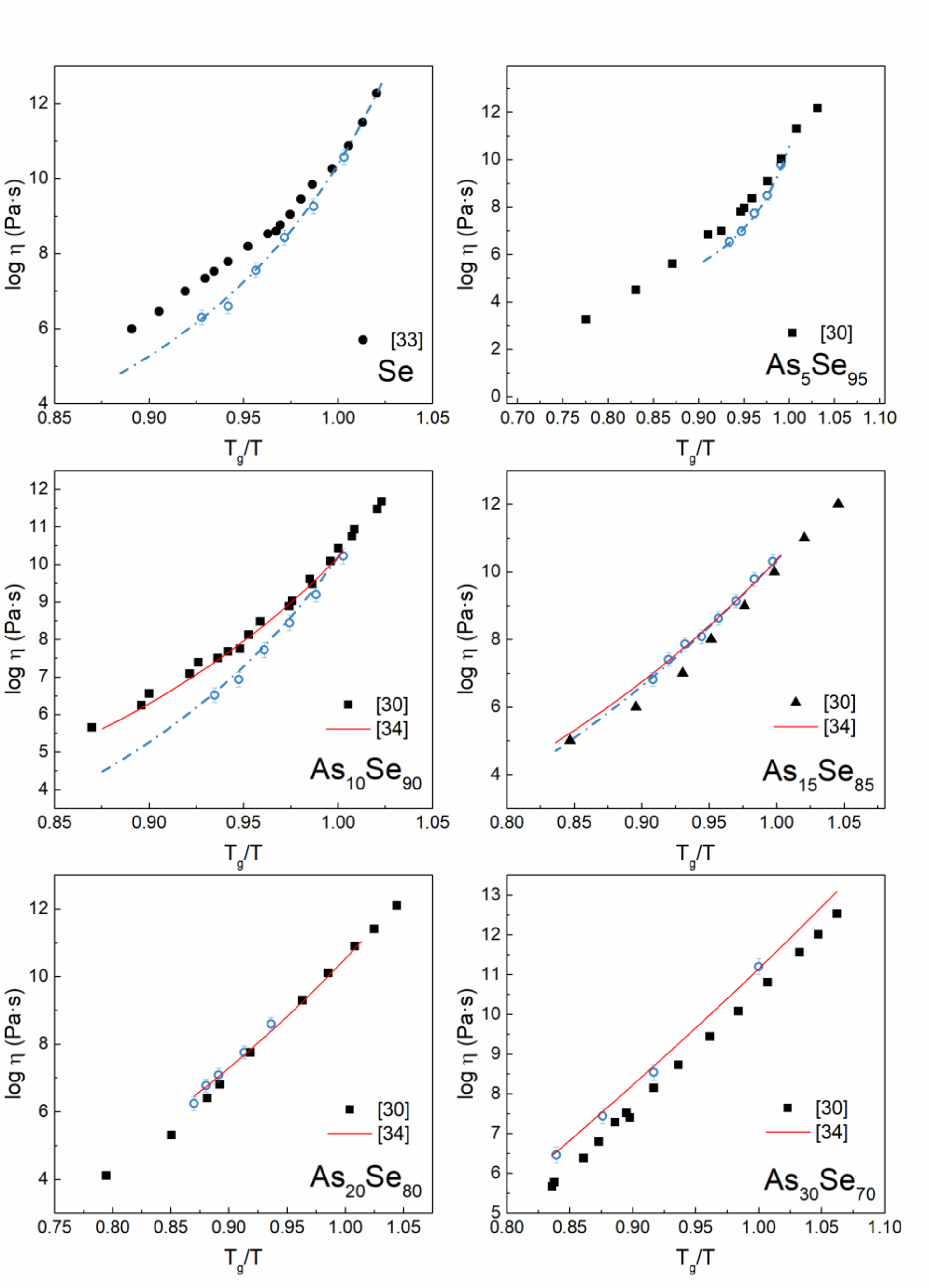
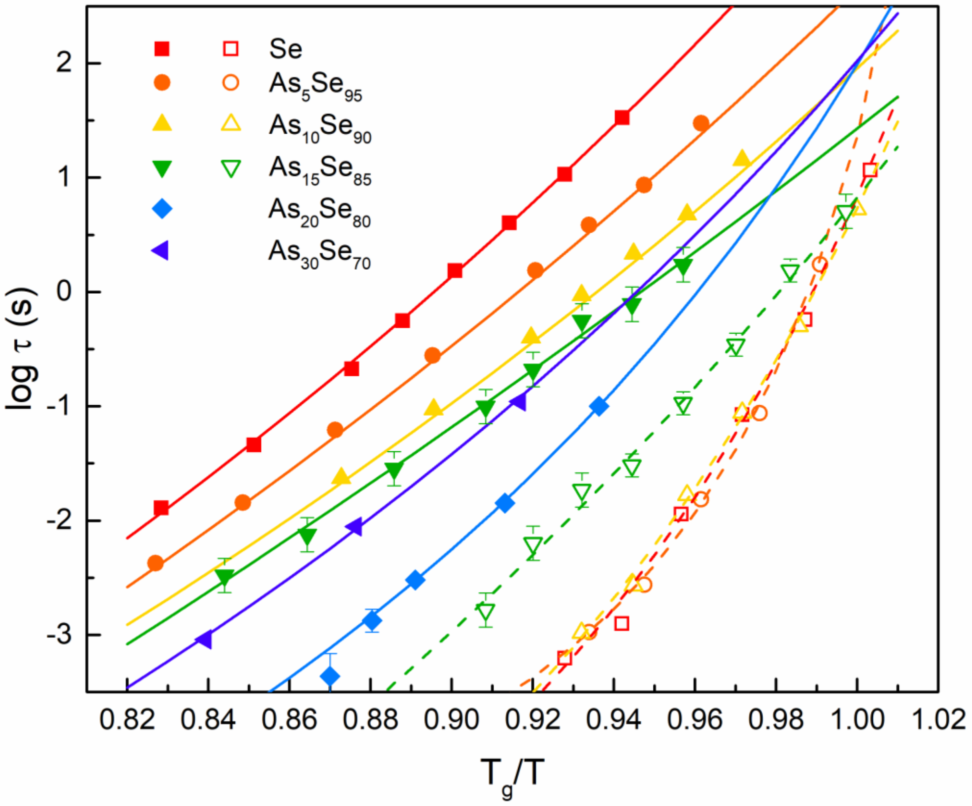

G', G" (Pa)
Angular frequency (rad/s)
60°C
70°C
80°C
90°C
100°C
110°C
As_5Se_{95}
As_5Se_{95} 100°C
G' and G" (Pa)
angular frequency (rad/s)
1
2
G'
G"
80°C
90°C
100°C
110°C
120°C
$As_{10}Se_{90}$
$As_{10}Se_{90}$ 120°C
150°C
$As_{20}Se_{80}$
$As_{20}Se_{80}$ 150°C
160°C
180°C
200°C
$As_{30}Se_{70}$
$As_{30}Se_{70}$ 200°C

Figure 2



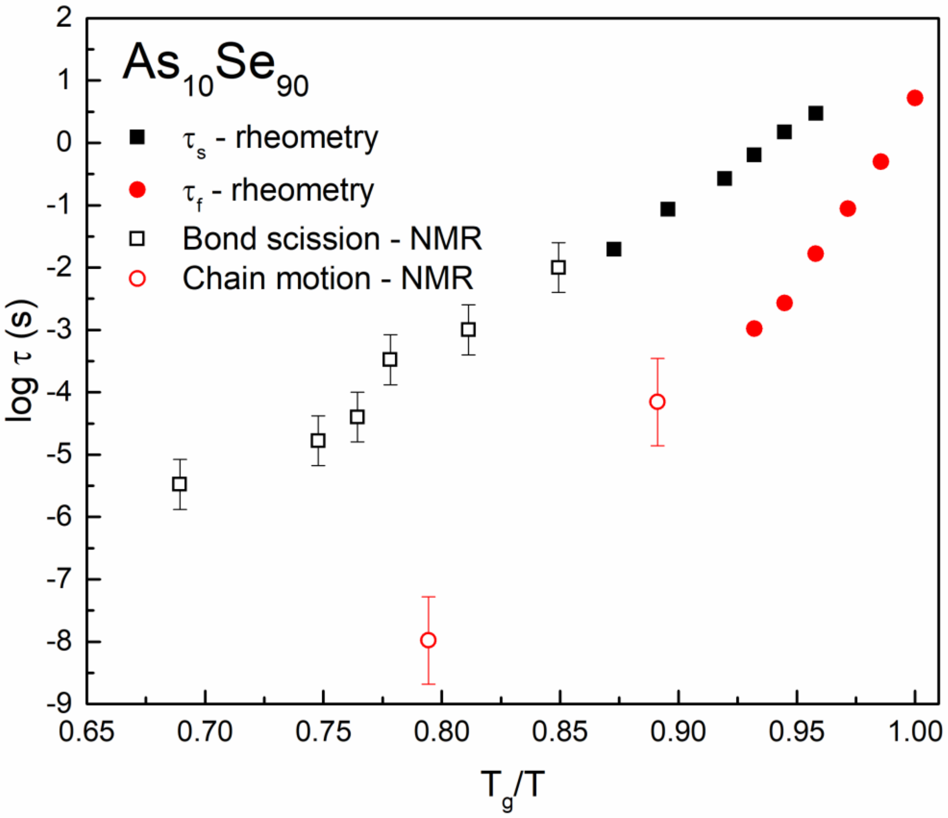
Se
[33]
As$_5$Se$_{95}$
[30]
As$_{10}$Se$_{90}$
[30]
[34]
As$_{15}$Se$_{85}$
[30]
[34]
As$_{20}$Se$_{80}$
[30]
[34]
As$_{30}$Se$_{70}$
[30]
[34]
log η (Pa·s)
T$_g$/T

Figure 3



Se
As_5Se_{95}
$As_{10}Se_{90}$
$As_{15}Se_{85}$
$As_{20}Se_{80}$
$As_{30}Se_{70}$
log τ (s)
2
1
0
-1
-2
-3
0.82
0.84
0.86
0.88
0.90
0.92
0.94
0.96
0.98
1.00
1.02
T_g/T

Figure 4



As$_{10}$Se$_{90}$
■ τ_s - rheometry
● τ_f - rheometry
□ Bond scission - NMR
○ Chain motion - NMR
log τ (s)
T_g/T
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00

Figure 5

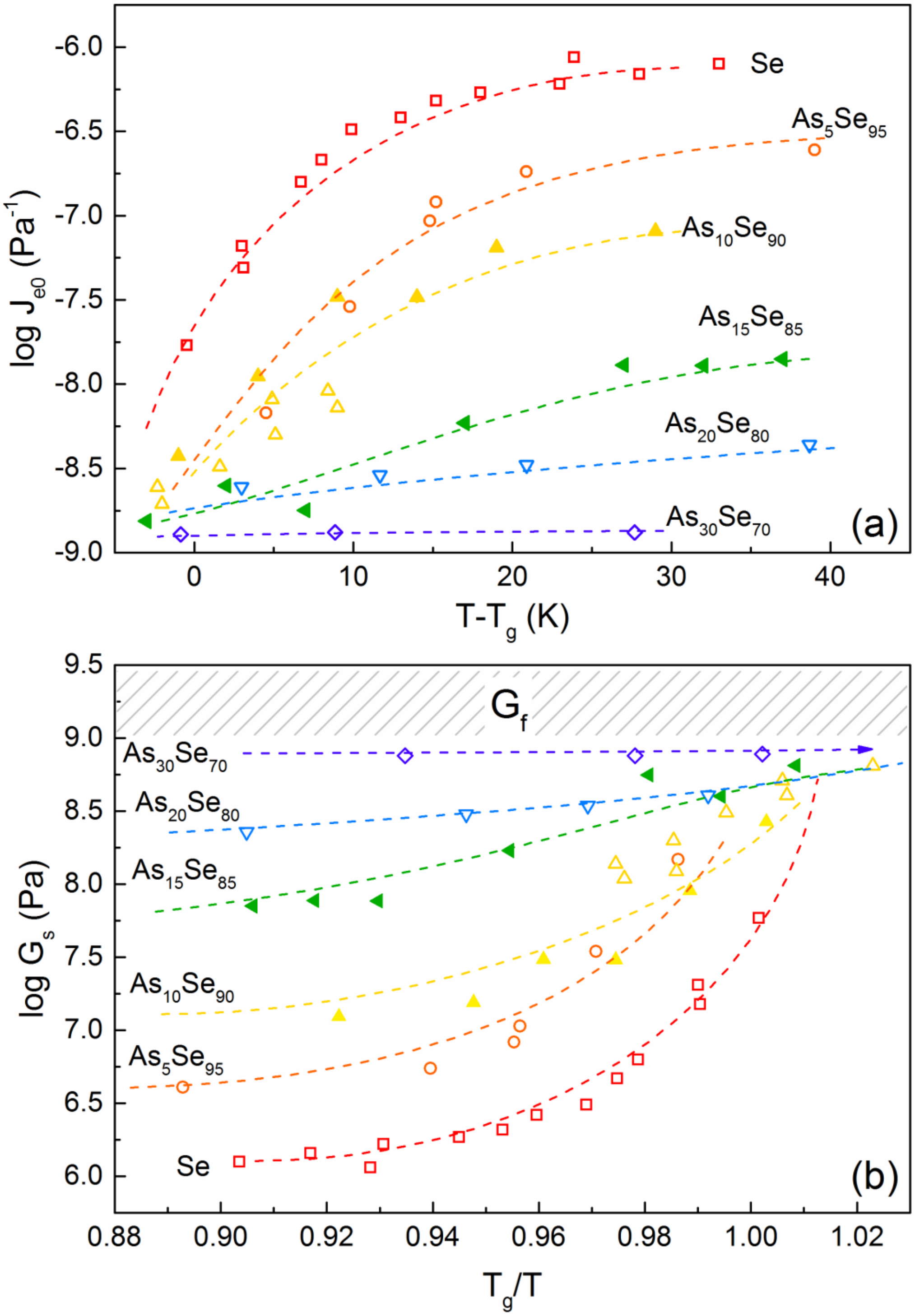
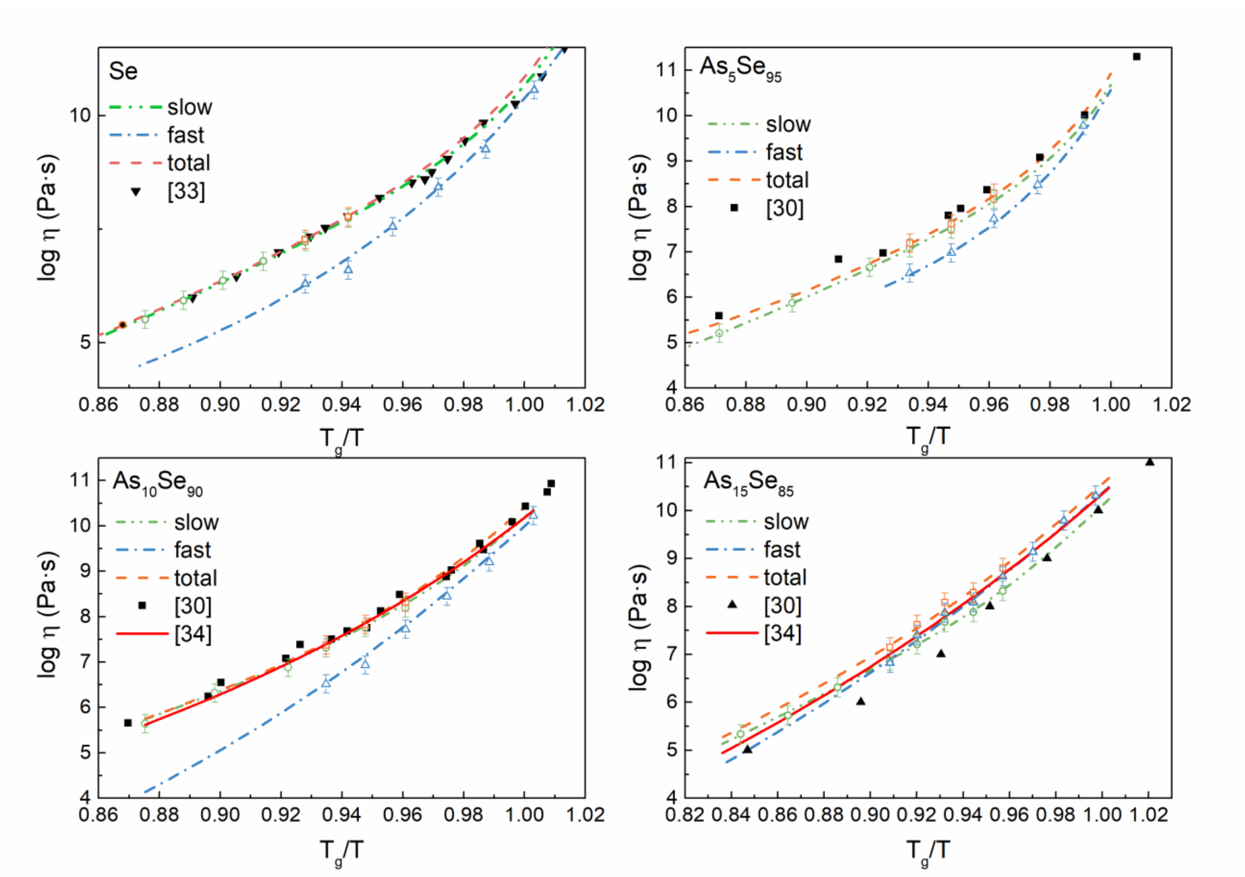

log J_{e0} (Pa^{-1})
-6.0
-6.5
-7.0
-7.5
-8.0
-8.5
-9.0
0
10
20
30
40
T-T_g (K)
Se
As_5Se_{95}
$As_{10}Se_{90}$
$As_{15}Se_{85}$
$As_{20}Se_{80}$
$As_{30}Se_{70}$
(a)
log G_s (Pa)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
G_f
$As_{30}Se_{70}$
$As_{20}Se_{80}$
$As_{15}Se_{85}$
$As_{10}Se_{90}$
As_5Se_{95}
Se
(b)
0.88
0.90
0.92
0.94
0.96
0.98
1.00
1.02
T_g/T

Fig. 6


Se
slow
fast
total
[33]
log η (Pa·s)
5
10
0.86 0.88 0.90 0.92 0.94 0.96 0.98 1.00 1.02
T_g/T
As_5Se_{95}
slow
fast
total
[30]
log η (Pa·s)
4 5 6 7 8 9 10 11
0.86 0.88 0.90 0.92 0.94 0.96 0.98 1.00 1.02
T_g/T
$As_{10}Se_{90}$
slow
fast
total
[30]
[34]
log η (Pa·s)
4 5 6 7 8 9 10 11
0.86 0.88 0.90 0.92 0.94 0.96 0.98 1.00 1.02
T_g/T
$As_{15}Se_{85}$
slow
fast
total
[30]
[34]
log η (Pa·s)
4 5 6 7 8 9 10 11
0.82 0.84 0.86 0.88 0.90 0.92 0.94 0.96 0.98 1.00 1.02
T_g/T