Fragility of One-dimensional Floppy Materials

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The fragility has worked as a fundamental concept characterising glass-forming liquids, whereas its atomic structural interpretation remains a challenge. We here examine viscosity behaviours in polyethylene (PE), S, Se and Te, which consist of distorted chain molecules with varied interchain strengths, in comparison with that in SiO_2, a typical strong material. Among the one-dimensional materials, S and PE appear also to be fairly strong. Such results suggest that the viscosity exhibits Arrhenius types if it is governed by single microscopic mechanisms such as Si-O bond scission or interchain slippages. On the other hand, Se and Te appear fragile with non-Arrhenius variations, which could be ascribable to mixed inter- and intra-chain interactions. Among these floppy materials, it is known that Se is the best glass former, the reason being discussed.

Keywords

fragility, topological structure, chain, floppy, supercooled liquid,

Conflict of Interest

The author declares no conflict of interest.

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1. Introduction

Glass science has ushered in unique concepts such as the glass transition, topological structural (floppy/rigid) change, and fragility (fragile/strong).[1,2] Among these, the fragility with a steepness index m, which works as a good metric characterizing the viscosity η (= 1/fluidity) variation with temperature T in (super-cooled) liquids,[3] has been grasped as an important parameter preluding the glass transition. Actually, extensive studies have been performed for uncovering and understanding relations between the index and other variables including density,[4] elasticity,[5,6] chemical composition,[7,8] enthalpy relaxation,[9] glass-transition temperature,[10-12] topological structure,[4,13-15] and stretched exponential factor.[16-18]

However, still elusive is the interpretation of the fragility in terms of microscopic structures. Are molecular liquids really fragile? How can a material become viscous (or fluid) with temperature changes in atomic structural scales? Regarding such problems, substantial studies using conceptual frameworks, e.g. the free-volume and energy-landscape models, have been presented.[9,13,19] For organic polymers, detailed studies have been performed on correlations between m and polymer structures, which possess varieties of chain lengths, backbones, and side groups.[6,10,11,17,20]. Are there alternative approaches for elucidating the fragility in atomic structural viewpoints?

We here consider for the first time the viscosities in simple one-dimensional polymeric liquids, PE, S, Se and Te. These one-dimensional materials, consisting of entangled covalent chains with the average atomic coordination number Z of two that are held together with weak interchain forces, are regarded as *floppy* in the topological term. Are these liquids really *fragile*, as commonly assumed? Or, more universally, are there any correlations between the topological structure and the fragility? The present work tries to shed light upon microscopic interpretations of the fragility. We also discuss glass-forming tendency in these materials.

2. Fundamentals

In brief, related backgrounds can be summarized as follows:[1,2,7,13,14] It is known that $\eta(T)$ in (super-cooled) liquids leading to the glass transition can be approximated using the Vogel-Fulcher-Tammann (VFT) equation;

$$\eta(T) = \eta_\infty \exp\{B/(T - T_0)\}, \qquad (1)$$

where η_∞ (= 10^{-4} P = 10^{-5} Pa·s) is an empirically-chosen viscosity at sufficiently high temperatures, B represents an activation temperature, and T_0 is referred to as the Vogel temperature, which appears to be nearly equal to the Kauzmann temperature T_K.[19] In Eq. (1), if $T_0 = 0$, it reduces to the Arrhenius type, an approximate form appearing in the so-called 'strong' liquid such as SiO_2. On the other hand, it has been known that molecular materials including salol and Se follow the VFT type with non-zero T_0, which are referred to as 'fragile'. Here, it is common to characterize the fragility using the steepness index m defined as;

$$m = [d(\log \eta)/d(T_g/T)]_{T = T_g}, \qquad (2)$$

where T_g (> T_0) is the glass-transition temperature, which is defined conventionally as $\eta(T_g) \approx 10^{13}$ P. Then, Eqs. (1) and (2) give $m = (BT_g/\ln 10)/(T_g - T_0)^2$, and in combination with the η_∞ and $\eta(T_g)$ values we have $T_0 = (1 - 17/m)T_g$ with $m \geq 17$ and $B (\equiv E_a/k_B) \approx 39(T_g - T_0)$.

3. $\eta(T_g/T)$ characteristics

Figure 1 shows the viscosity η as a function of T_g/T, the so-called Angell plot, and Table 1 lists related parameters in SiO$_2$, PE, S, Se and Te. Some comments may be in order for these materials. Regarding SiO$_2$, the network structure consisting of three-dimensional corner-sharing SiO$_{4/2}$ units is established,[1,2,21,22] and $\eta(T_g/T)$ curves with $m \approx 25$ have reproducibly been obtained.[10,14,16] Besides, for liquid and glassy Se, it has been known that the atomic structure is composed mainly with distorted chain molecules[2,22-25] with an estimated atomic number of $10^5 - 10^6$ at the melting temperature T_m (= 494 K).[2,26,27] And, $\eta(T_g/T)$ with $T_g \approx 310$ K, leading to $m \approx 65$, has also been reproduced.[28-32] Incidentally, note that throughout the present analyses, the accuracy of m is estimated at about ±5, due to limited temperature ranges of $\eta(T_g/T)$ data and so forth.
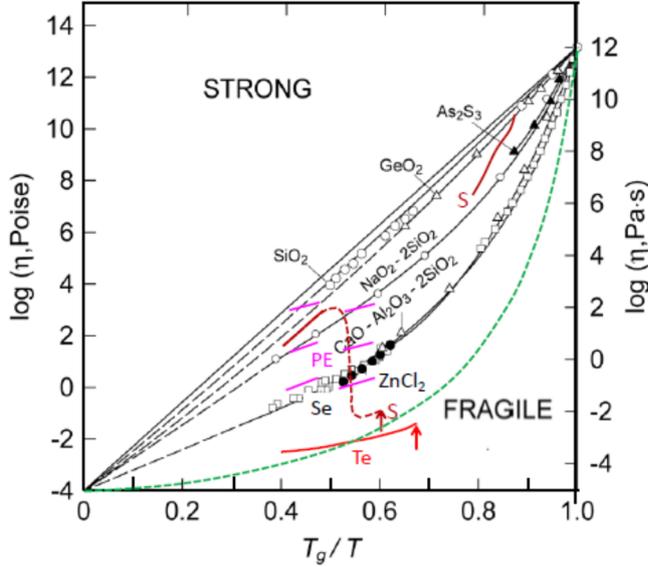
On the other hand, the situation for S is complicated.[5,31,33-35] The reason is ascribable to the two factors; crystallizable tendency of S$_8$ ring molecules and existence of the polymerization temperature T_λ at 159 °C (= 432 K > $T_m \approx 390$ K),[31,35-37] which appears in Fig. 1 as the η drop at $T_g/T \approx 0.55$. It is generally assumed that below and above the temperature, respectively, the liquid consists of S$_8$ molecules and contains chain molecules with varied atomic numbers;[5,23,37] e.g. $10^4 - 10^6$ at ~440 K,[38,39] which are assumed to govern the viscosity of a super-cooled state at $T_g/T \approx 0.8$.[5,38,40,41] We also adopt $T_g \approx 240$ K (Table 1) for S chain glasses,[42] the resulting $\eta(T_g/T)$ being plotted in Fig. 1 by two, solid brown lines at $T_g/T \approx 0.45$ and 0.8.

Fig. 1. Viscosities $\eta(T_g/T)$ for SiO$_2$ and Se,[2] with additions of S (brown),[38,40,41] Te (red),[48] and PEs (violet)[59] with $n \approx 300, 800,$ and 2000 (from low to upper) for $T_g = 200$ and 250 K (left and right). Arrows indicate T_m positions, and a dashed green line shows the η variation with $m = 150$.

Probably reflecting such structural features, reported m's thus far appear confusing, which needs to be fixed. Based on a previous η result at $T_g/T \approx 0.8$,[41] Ruta et al.,[5] assuming two relaxation processes arising from segmental flow and bond interchange, suggest $m \approx 28 - 435$, the latter being too high as commented. Recently, Chen et al.[31] put forward a high value of $m = 126$ and $T_0 \approx 203$ K (Table 1) through analyses of crystallization kinetics in bulk samples, which may be compatible with the dashed brown line in Fig. 1 for S$_8$ liquids, since their samples are quenched from ~400 K ($T_g/T \approx 0.6$), below T_λ. (It should be noted however that $T_g \approx 240$ K is assigned for S-chain glasses, and accordingly, the horizontal position of $\eta(T_g/T)$ for S$_8$-ring liquids in the figure is tentative.) Further, Yuan et al.[35] obtain $m \approx 35$ and 150 for the liquids above and below T_λ. Unfortunately, their $\eta(T_g/T)$ (and also in Ref. 34) is plotted higher by an order than the original ones,[38,40,41] which is corrected in Fig. 1, and an approximate curve fitting gives rise to $m \approx 30$ for S-chain liquids. Note that this value appears to be consistent with m variation (= 30 − 60) in the Ge$_x$-S$_{100-x}$ system with $30 \leq x \leq 44$.[43]

Table 1. Related parameters reported (with references superscripted) and estimated in the present (with no superscript) in the five materials; melting temperature T_m, glass-transition temperature T_g, Vogel temperature T_0, steepness index m, activation energy E_a calculated from $E_a \equiv k_B B \approx 39 k_B (T_g - T_0)$, bond strength E_r, bond length r, interchain atomic distance (in related crystals) R, and ratios T_g/T_m and R/r. Note that R in a liquid seems to be slightly longer than that in the crystal, while the table lists the crystalline R, since the liquid R cannot be fixed.

material	T_m [K]	T_g [K]	T_0 [K]	T_g/T_m	m	E_a [eV]	E_r [eV]	r [Å]	R [Å]	R/r
SiO$_2$	1883[a]	1463[b] 1500[c,d]	139[e]	0.8	20[c] 28[d]	4.4	3.8[g]	1.62[f]	x	x
PE	373-411[h] 415[i]	200[j] 230[l] 237[m] 252[h]	180[n] 120-160[i] ~150	0.56	46[j,c,k] ~40	0.3	3.6[g]	1.54[l]	~4[l]	~2.6
S	390[a,s]	~235[m] 243[n] 246[o] 276[q]	203[p] ~100	0.62	126[p] 28, 86, 435[q] 35, 150[r] ~30	0.5	2.76[s,t]	2.1[s,v]	3.5[s,v]	1.7
Se	494[a,s]	305[c] 308[d] 313[b]	~260[u] 240[p]	0.63	62[j] 64[u] 68[p]	0.2	1.91[s] 2.2[t]	2.37[s,v,t]	3.44[s,v]	1.45
Te	723[a,s]	482?	427?	0.66?	~150	0.2	1.69[s]	2.83[s,v,x]	3.49[s,v]	1.23

[a]D.R.Lide (ed), *CRC Handbook of Chemistry and Physics,* 74th ed. Boca Raton, **1993**. [b][22], [c][10], [d][25], [e][8], [f][21], [g][73], [h][57], [i][58], [j][17], [l][66], [i][59], [j][9], [k][11], [l][62], [m][33], [n][42], [o][41], [p][31], [q][5], [r][35], [s][36], [t][23], [u][7], [v][51], [x][52].

To the author's knowledge, it is quite difficult if not impossible to vitrify Te.[44-46] However, since $\eta(T)$ data in the liquid state are available[47-49] and atomic structures of liquid and amorphous Te have been demonstrated to be composed by entangled chains,[50-52] it would be valuable to examine the behavior. Actually, $\eta(T)$ at $T \approx 723 - 1200$ K for liquid Te can be calculated from kinematic viscosity and density reported by Li et al.,[48] the result being seemingly in quantitative consistency with other data.[47,49] On the other hand, the glass-transition temperature cannot be fixed straightforwardly. It is known that amorphous Te films deposited upon cooled substrates crystalize at ~285 K,[53] *without undergoing glass transition*. We then tentatively follow the empirical rule $T_g \approx (2/3) T_m$[1,2] with $T_m = 723$ K,[44] which gives $T_g \approx 480$ K, and obtain the $\eta(T_g/T)$ curve in Fig. 1 with $m \approx 150$, which appears rather high. For instance, it is reported that $m \approx 60 - 81$ in the Se$_x$Te$_{100-x}$ (x ≥ 30)[30] glass system, $42 - 120$ in Ge$_{15}$Te$_{85}$,[54] and 90 and 129 in Ge$_2$Sb$_2$Te,[54,55] Herein, one might argue that the selected T_g (≈ 480 K) is appreciably higher than those (~350 K) obtained through extrapolations from T_g variations in the Se$_x$Te$_{100-x}$ (x ≥ 30),[30] As$_x$Te$_{100-x}$ (x ≥ 25),[56] and Ge$_x$Te$_{100-x}$ (x ≥ 10)[56] systems. Nevertheless, a lower T_g would not provide a marked change in the m value, since it only shifts the $\eta(T_g/T)$ curve horizontally a bit (by ~350/480) to the left-hand side in Fig. 1. In short, it seems reasonable to take $m \approx$ 150, or $m \geq$ 100; i.e., very fragile.

Situations for PE are also not straightforward due to diverse polymer structures.[57,58] The atomic structure

consisting of -(CH$_2$)$_n$- chains can vary in the polymerization degree n and chain branching. Besides, the material is also crystallizable. For the viscosity, Pearson et al.[59] have demonstrated that it dramatically increases ($\eta \approx 10^{-2} - 10^3$ P at 450 K) with an increase in n from 16 to 2000, which corresponds to the molecular weight of $M_w \approx 10^2 - 10^4$ g/mol, since $M_w \approx 14n$. Theoretically, it is known that viscoelastic properties of PE with n lower and higher than 10^2 could be analyzed on the basis of Rouse and reptation models,[60] respectively. And, Tries et al.[61] have succeeded to reproduce the experimental $\eta(T)$ at $T \approx 450 - 500$ K for a sample of $n = 70$, applying a Monte-Carlo calculation to the Rouse model, which takes thermally-activated Gaussian segmental motions into account. More recently, some researchers are challenging molecular dynamic (MD) analyses in longer chains with $n = 96 - 2000$ using the reptation model,[62-64] in which chain motions are topologically constrained by entanglement. However, no comparisons with experimental $\eta(T)$ seem to be performed. On the other hand, for determination of T_g, no viscosity data are available, to the author's knowledge. Instead, several experimental studies obtained $T_g \approx 200 - 250$ K (Table 1), which tends to increase with the chain length n.[11] In accordance, MD simulations for volume changes of PE with $n = 300$ and 768 give $T_g \approx 200$ and 230 K, respectively.[65,66]

Taking these backgrounds into account, we plot in Fig. 1 the viscosities in PE samples[59] of $n = 300$, 800, and 2000 using $T_g \approx 200$ and 250 K. Or, more precisely, a plausible situation may be $T_g \approx 200$ K for $n = 300$ (lower-left curve in the figure) and 250 K for 2000 (upper-right). The result demonstrates that PE becomes stronger with the chain length, consistent with observations in other polymers.[11] We also take $m \approx 40$ for a typical PE sample of $n = 2000$, since the curve overlaps at $T_g/T \approx 0.6$ with that of NaO$_2$·2SiO$_2$ assigned to $m \approx 40$,[8,10,16] despite of different gradients, which may arise from restricted experimental conditions.[59] Note that previous studies have adopted a similar value of 46, which was estimated from dielectric loss spectra.[9,10,11,17]

In short, despite the uncertainties noted above, Fig. 1 manifests that, even among the simple one-dimensional floppy materials, the fragilities are substantially different. PE and S-chain liquids appear to be more-or-less 'strong' with $m \approx 35$, whereas Se and Te (and S$_8$) are 'fragile' with $m \approx 65 - 150$. How can we interpret such fragility difference among the floppy materials, having the same topological structure?

4. Discussion

At the outset, it may be instructive to recall the situation in SiO$_2$. For liquid SiO$_2$, it is un-doubtful that the scission of Si-O bonds induces the fluidity throughout the temperature range of interest,[21] the view being consistent with the nearly Arrhenius behavior with $E_a \approx 4.4$ eV that is greater than the bond strength E_r of 3.8 eV (Table 1). And, Equation (2) suggests that the small m value of ~25 is governed by the high T_g ($\gg T_0$) arising from rigid three-dimensional networks.

Following this idea, we assume that the Arrhenius-like viscosities in PE and S appear through a *single* mechanism, which is possibly chain motions that are modeled by reptation theories.[34,62-64] The covalent bonds with the strengths of ~3 eV (Table 1) could be intact with no chain scission and crossing, as commonly assumed for organic polymers.[11,20] With respect to Equation (2), the small m's of ~35 are possibly governed by weak interchain interactions appearing as E_a (= $k_B B$) ≈ 0.4 eV, which compensates the low T_g (~230 K) arising from floppy structures with the low coordination of $Z = 2$.[67]

On the other hand, it is tempting to assume that the non-Arrhenius behaviors in Se and Te are sustained by, at

least, two kinds of atomic mechanisms. One is the inter-chain slippage, as above, and the other is intra-bond scission/exchange; the latter being consistent with small bond strengths of $E_r \leq 2$ eV (Table 1) and also with structural models assuming ring-chain coexistence.[25,26] (It is also known that the bond scission in Se occurs efficiently under photo-excitation.[69]) The large m's with $65 - 150$, indicating high fragility, are ascribable in Equation (2) to moderate E_a (≈ 0.2 eV) and high T_0 ($< T_g$), which may be determined by the two factors; one is the inter- and intra-bond mixing, in consistency with small R/r, and the other is temperature variations of the chain slippage and breakage. Note that the contribution of the two mechanisms to viscous behaviors in S and Se has been suggested,[5,70] although the details could be different.

In support of the present idea, we see in Fig. 2 a close correlation between m and the bond energy E_r. The index m monotonically decreases with an increase in E_r, or very roughly $m \sim E_r^{-2}$, which is *irrespective of the topological structures* possessing the one- and three-dimensional connectivity. In fragile (high m) chain liquids the atomic bonds are likely to be broken at around T_g, where m is defined. Alternatively, provided that m were defined at high temperature limits, not at T_g, it might exhibit a correlation with intermolecular strengths. Nevertheless, it seems difficult to examine such correlation because the intermolecular strength is assumed to vary with segmental lengths and so forth.
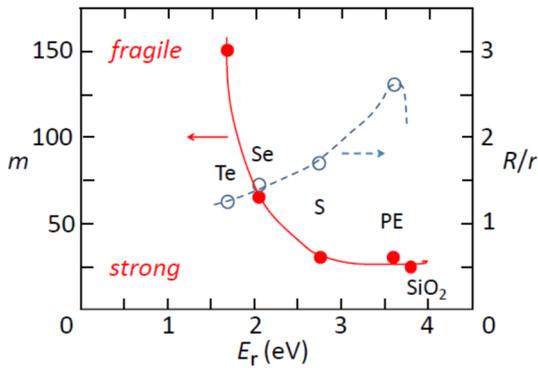
Incidentally, are there any effects of chain stiffness on the fragility in these simple materials? The stiffness could be governed by the chain torsion, since its force constant is substantially smaller than those of two- and three-body atomic vibrations.[2,22,23] And, it is plausible that the torsional barrier becomes lower from PE to Te,[71] although the absolute values (~ 0.1 eV) being quantitatively diverse.[61,62,72,73] Despite that, it seems that PE chains are fairly rigid, or the segments are much longer than those in Te. Such difference possibly affects Rouse-type and/or reptational motions of the chains, while the effect could be smaller than that by the intra-bond scission and/or exchange, which should be examined quantitatively.

Fig. 2. The fragility m and a distance ratio R/r as a function of the covalent bond strength E_r (the data from Table 1).

Finally, we may wonder why PE, S and Te are likely to crystallize and only Se can form a relatively stable glass. A rough sketch could be drawn as follows: PE is likely to crystallize due to highly diffusive segmental motions arising from low friction of interchain interaction and highly packable chain structures with no side groups. S easily crystallizes, reflecting the existence of the most stable, stackable, small S_8 ring molecules. And, Te cannot vitrify because of nearly isotropic ($R/r \approx 1.23$), metallic bonds. By contrast, in Se, the lowest-energy molecular form is the helical chain, the mixture being held together by moderately-mixed inter- and intra-chain forces giving rise to $R/r \approx 1.45$. The entangled chain structure actually provides greater residual (configurational) entropy of 3.6 J/(K·mol)[74] in comparison with 2.6 J/(K·mol)[75] in PE, which could be favorable to its subtle glass formation.

5. Summary

The present work manifests that the floppiness and the fragility do not necessarily correlate in simple

one-dimensional materials. Though some data are limited in the temperature ranges, it appears that S and PE are rather strong, while Se and Te are fragile, the result revealing that the topological connectivity ($Z = 2$) alone cannot determine the fragility. Otherwise, these observations could be ascribed to different degrees of intra- and inter-chain bond strengths. In the strong liquids, intra-chain bonds are assumed to be intact, and only chain/segment slipping governs the viscosity. By contrast, in the fragile, in addition to the inter-chain motion, weak intra-chain bonds are likely to be broken and/or exchanged. It is speculated that such twofold interactions with moderate anisotropy causes the high fragility, and also the glass formation in Se.

The present idea on the one-dimensional liquids may be extended to zero- and two-dimensional materials. For instance, it has been demonstrated that small molecules, e.g., ortho-terphenyl are fragile with $m \approx 80$,[6,7,10,14,16] but the character may be affected by intra-molecular relaxations. Are *elemental* van-der-Waals fluids such as Ar also fragile? Examinations using MD simulations will be tempting.

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