

**Response to “Comment on ‘Molecular origin of aging of pure Se glass: Growth of inter-chain structural correlations, network compaction, and partial ordering’” [J. Chem. Phys. 148, 157101 (2018)]**

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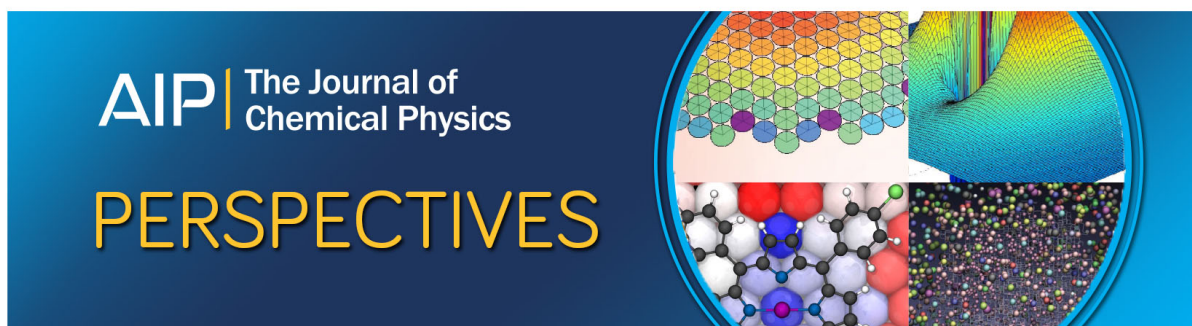
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## Response to “Comment on ‘Molecular origin of aging of pure Se glass: Growth of inter-chain structural correlations, network compaction, and partial ordering’” [J. Chem. Phys. 148, 157101 (2018)]

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In their comment, Shpotyuk *et al.*<sup>1</sup> raised a question on possible broadening in the width of  $T_g$ ,  $W$ , and/or even  $T_g$  bifurcation upon aging in Se-rich  $Ge_xSe_{100-x}$  glasses if  $Se_8$  crowns are decoupled from a glass backbone. Dash *et al.*<sup>2</sup> examined pure Se as well as Se-rich  $Ge_xSe_{100-x}$  glasses and, based on their modulated differential scanning calorimetry (MDSC) results, found the width  $W$  to narrow by almost a factor of 6 in a pure Se glass and Se-rich glasses ( $0 < x < 6\%$ ) upon RT aging for 18 months. In the same range ( $0 < x < 6\%$ ) of Se-rich glasses, Dash *et al.* also observed an aging induced increase of  $T_g$ , which displays a maximum near  $x = 3\%$ . At higher  $x$  ( $6\% < x < 10\%$ ), Dash *et al.* found the aging induced narrowing of  $W$  to steadily decrease and to vanish near  $x = 10\%$ . And at still higher  $x$  ( $10\% < x < 20\%$ ),  $W$  increases almost linearly with  $x$ , as rigidity in the network percolates near  $x = 20\%$ .

Although bimodal  $T_g$ s have been reported for some Se-rich  $Ge_xSe_{100-x}$  glasses as a result of long-term aging ( $>13$  yr),<sup>3,4</sup> Dash *et al.*<sup>2</sup> observed unimodal  $T_g$ s in all their Ge–Se glasses (both fresh and aged for 18 months). The variation of  $T_g(x)$  in the  $0\% < x < 10\%$  range for the Ge–Se binary is quite linear in  $x$ . A unimodal  $T_g$  would mean that the Ge:Se stoichiometry “ $x$ ” is the *same* across a batch composition. And as  $Se_8$  rings decouple from the backbone, one expects  $T_g$  to increase uniformly across a sample as the connectivity of the Ge-rich backbone increases. But this would not be the case if the rejuvenated sample were to have a stoichiometry variation “ $x$ ” across the batch displaying more than one  $T_g$ . We have compared the  $T_g$  endotherms of the glass samples of Dash *et al.* at  $x = 4\%$  and  $8\%$  with those of Saiter *et al.*<sup>3</sup> in DSC measurements, each taken at  $20^\circ\text{C}/\text{min}$ , and found the  $T_g$  widths of the glasses of Dash *et al.* to be noticeably narrower than those of Saiter *et al.* The finding is consistent with the synthesis employed; Saiter *et al.* alloyed their batches at  $1000^\circ\text{C}$  for 10 h, while Dash *et al.* alloyed their 2-g batches at  $950^\circ\text{C}$  for 7 days. Dash *et al.* confirmed the homogeneity of their melts/glasses from Raman profiling experiments. These findings suggest that the broadening or bifurcation of  $T_g$  of the aged glasses is tied to melt/glass heterogeneity.

Shpotyuk *et al.*<sup>1</sup> questioned why does the width of  $T_g$  of Se-glass narrows upon aging when the glass decouples into polymeric  $Se_n$  chains and  $Se_8$  rings and becomes more disordered? When  $Se_8$  rings *decouple* from the backbone of polymeric  $Se_n$  chains, these *do not* contribute to the connectivity of the backbone. Dash *et al.*<sup>2</sup> showed that in these covalently bonded glasses the magnitude of  $T_g$  and the width of  $T_g$  are controlled respectively by the connectivity and degree of structural ordering of the super-flexible polymeric  $Se_n$  chains. Specifically, aging leads *interchain* structural ordering mediated by the *secondary*  $\pi$ -like *non-bonding* interactions to grow at the expense of the *primary*  $\sigma$ -like *intrachain bonding* ones and leads chains to compact and come together (Fig. 16 and Sec. III of Ref. 2). The process leads to a decrease in the configurational entropy of the glass, which leads to an increase in the non-reversing enthalpy. Upon aging, some chains correlate enough to form the *nuclei* of the trigonal(t)-Se, which then eventually grow to form the t-Se phase in a measurable amount ( $\sim 10\%$ ) only after 18 months of aging in the dark at 300 K in a Se glass to be detected in Raman scattering and powder x-ray diffraction experiments (Figs. 7 and 8 Ref. 2). Thus, room temperature aging of a Se glass for waiting times exceeding 18 months will have significant concentrations of t-Se.

Gulbitten *et al.*<sup>5</sup> have examined the “Enthalpy of relaxation in pure Se” as a function of aging over a 2-week period at  $25^\circ\text{C}$  by recording the *complex specific heat* (the *real*  $C_p'$ , and *imaginary*  $C_p''$ ) in an MDSC experiment. Specifically, the authors elegantly elucidated the *width of the imaginary part of the specific heat*,  $C_p''$ , the main thrust of their work, as also suggested by the title of the paper. Gulbitten *et al.* observed the width in  $C_p''$  to decrease upon aging at 300 K, which was taken as evidence of a *narrowing of fluctuations in the enthalpy of relaxation*. These authors did not comment on the width of  $T_g$  due to aging. We stand behind our claim<sup>2</sup> that the width of  $T_g$  of a 4 months room temperature aged Se glass is  $1.5^\circ\text{C}$ .

In their comment, Shpotyuk *et al.*<sup>1</sup> found the new topological threshold near  $x = 3\%$  in the  $Ge_xSe_{100-x}$  glasses, corresponding to a mean coordination number of  $\langle r \rangle = 2.06$  showing a maximum in  $T_g$  upon aging to be “very controversial.” The state of a glass can be directly captured by a measurement of the non-reversing enthalpy of relaxation that is established in MDSC unambiguously.  $T_g$  “onset” and “end” points in an

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MDSC experiment, a technique which makes use of rather slow scan rates (1/3rd °C/min–3 °C/min) and long modulation time ( $t = 100$  s), overcome thermal inertia of the head or kinetic shifts due to scan rates.<sup>6</sup> This is in sharp contrast to DSC, where not only  $T_g$  “end” but even  $T_g$  “onset” are, indeed, up-shifted in temperature because of the much higher scan rates used, ranging from 10 °C to 40 °C/min, almost an order to two orders of magnitude higher than in MDSC. One can *uniquely* separate<sup>2</sup> the *enthalpy of relaxation* from  $T_g$  in MDSC, but such a separation is difficult in a DSC experiment. Shpotyuk *et al.*<sup>1</sup> are quite correct in recognizing the challenges that high scan rates in a DSC experiment bring on issues of heat transfer from the calorimeter head to the sample and the inability of the glass to relax quickly enough at  $T_g$  to track the imposed scan rates. It is precisely because of these considerations that in a DSC experiment the peak in the enthalpy of relaxation of a fresh Se glass occurs at 45.4(3) °C but then upshifts to 52.5(3) °C upon 4-month aging, even though the  $T_g$  of *both* the *fresh* and the *aged* glasses remains unchanged at 40.6(5) °C, as established from the MDSC reversing heat-flow (Figs. 2 and 5 of Ref. 2).

The new topological threshold reported near  $x = 3\%$  in aged Ge–Se glasses corresponds to a maximum in  $T_g$  that is driven by the underlying decoupling of  $Se_8$  rings from the glass backbone, which renders it Ge-richer or more connected. The effect is generic to Se-rich ( $x < 6\%$ ) glasses. In the  $Ge_xSe_{100-x}$  binary, it corresponds to a compromise composition between  $x = 0\%$  Ge and  $x = 6\%$  Ge. At  $x = 0\%$ , i.e., in pure Se, although much decoupling of  $Se_8$  rings takes place upon aging, the  $T_g$  of the glass remains *unchanged* because the connectivity of the polymeric  $Se_n$  chains comprising the backbone remains fixed at  $r = 2$  always. Here the coordination number,  $r$ , a measure of network connectivity, provides a direct measure of  $T_g$  of the covalently bonded Se glass, as recognized in stochastic agglomeration theory.<sup>7</sup> At  $x = 6\%$ , the decoupling of  $Se_8$  rings from the shortened  $Se_n$  chain segments between the Ge cross-links is precluded because chains are now shorter, i.e.,  $n \leq 8$ . These ideas lead in a natural way to the topological threshold near  $x = 3\%$  in the present Ge–Se glasses, where the effect of  $Se_8$  decoupling reveals the largest increase of  $T_g$ . In a binary  $Ge_xSe_{100-x}$  glass, the mean coordination number  $\langle r \rangle = 4x + 2(1 - x) = 2(1 + x) = 2.06$  at  $x = 0.03$ . Such a topological threshold has also been observed in Se-rich binary  $As_ySe_{100-y}$  glasses (Fig. 5 of Ref. 8) near  $y = 6\%$  or  $\langle r \rangle = 2 + y = 2.06$ , i.e., the same connectivity, as in Ge–Se glasses.

Another issue brought forward by Shpotyuk *et al.*<sup>1</sup> is that aging experiments on Ge–Se glasses in Ref. 5 were not performed at the same  $T_a/T_g$ . Here  $T_a$  represents the temperature where aging was examined. In the aging induced changes of the enthalpy of relaxation  $\Delta H_{nr}$  and the width  $W$  of  $T_g$  for pure Se (Figs. 5 and 6 of Ref. 2), we found that  $T_g$  remains unchanged near 40.6(5) °C as the glass ages at  $T_a = 23$  °C. Thus, the ratio in  $T_a/T_g$  for the case of a pure Se glass is 0.95 and does not

change upon aging. However, in the Se-rich glasses, in the  $0\% < x < 6\%$  range, the ratio  $T_a/T_g$  will decrease somewhat from 0.95 to 0.89 as  $x$  increases to 6% of Ge and  $T_g$  increases. The kinetics of aging would be somewhat slower near  $x = 6\%$  than at  $x = 0\%$ . But given that Dash *et al.*<sup>2</sup> examined aging over long waiting times,  $t_w$  of 4 months, and separately of 8 months, the observed global trends of aging in the width ( $W$ ), enthalpy of relaxation ( $\Delta H_{nr}$ ), the glass transition temperature [ $T_g(x)$ ], and the upshift in  $T_g$  due to aging at a given ‘ $x$ ’,  $T_g(t_w) - T_g(0)$  in these Se-rich glasses are well documented from the results (Fig. 4 of Ref. 2).

The Raman mode assignments of  $Se_n$  chains and  $Se_8$  rings in Se-glass and Se-crystal are well documented from previous work<sup>9,10</sup> (see Table II of Ref. 2). In deconvoluting the broad band centered near  $250\text{ cm}^{-1}$  in the Se glass ( $x = 0$ ) and Se-rich glasses ( $x \leq 10\%$ ) in terms of a trimodal distribution, we imposed *no constraints* (to ascertain the uniqueness of the deconvolution) on either mode-centroid, mode-width, or mode-scattering strength except using a Voigt profile with a 95%:5% mix of Gaussian to Lorentzian. The most striking result we carried away from these results (Fig. 12 of Ref. 2) is *nearly 24% reduction* in FWHM of the B-mode (uncorrelated  $Se_n$  chains) of Se glass ( $x = 0$ ) upon 8 months of aging at 300 K, a finding that reinforces the growth in structural ordering of the uncorrelated  $Se_n$  chains as the central mechanism of aging. The results also reveal a small red-shift of the correlated  $Se_n$  chain mode frequency and a blue-shift of the uncorrelated chain-mode frequency but no measurable shift of the B-mode frequency. The exact reason for these small shifts is not entirely clear at this stage. Finally, the Raman results also reveal that an aging induced reduction in the fraction of  $Se_8$  rings [Fig. 15(c) of Ref. 2] at the expense of uncorrelated  $Se_n$  chains [Fig. 15(b) of Ref. 2] occurs as Ge is alloyed in the base Se glass, a result that is fully consistent with the Ge cross-linking of polymeric  $Se_n$  chains and with the length of the  $Se_n$  chains segments “ $n$ ” between Ge cross-links decreasing as Ge content “ $x$ ” of the binary glasses increases (Fig. 17 of Ref. 2).

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