Fragility of Ge-As-Se Glass-Forming Liquids in Relation to Rigidity Percolation, and the Kauzmann Paradox

M. Tatsumisago,(1) B. L. Halfpap,(2) J. L. Green,(1) S. M. Lindsay,(2) and C. A. Angell(1)
(1)*Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604*
(2)*Department of Physics, Arizona State University, Tempe, Arizona 85287-1604*

(Received 18 December 1989)

The concept of mean-field rigidity percolation at average coordination number $\langle r\rangle = 2.4$ in covalently bonded inorganic glasses is shown to be relevant to the liquid-state behavior of glass-forming chalcogenide systems. In particular it correlates with remarkable variations in "fragility" and excess heat capacity which we observe in the model ternary system Ge-As-Se. Except near As_2Se_3, T_g itself depends only on $\langle r\rangle$ anywhere in the system up to $\langle r\rangle = 2.5$. These findings provide an important link between key structural concepts of glass science, the relaxation phenomena, and the thermodynamic problem embodied in the Kauzmann paradox.

PACS numbers: 61.42.+h

The notion that covalent bonding in glasses may be optimized when the average coordination number ($\langle r\rangle$) is 2.4 was advanced first by Phillips[1] to explain the strong glass-forming propensity of some chalcogenide systems. It was later refined by Thorpe,[2] who predicted, for the mean-field case, a sudden rise in bulk modulus as the composition in binary or multicomponent systems passes through the "rigidity percolation" (or vector percolation) threshold at this same coordination number.

Some sound-velocity-based observations supporting the idea of rigidity percolation were presented in an earlier Letter on the model system Ge-As-Se.[3] This system was chosen because the bonding numbers (valences) of 4, 3, and 2, respectively, permit realization of $\langle r\rangle = 2.4$ at many different chemical compositions ($\langle r\rangle = 4X_{Ge} + 3X_{As} + 2X_{Se}$, where X is mole fraction). This permits separation of connectivity effects from chemical effects.[3] However, these early measurements were later found to be affected adversely by oxide contamination of the samples. In fact, the absence of a transition at $\langle r\rangle = 2.4$ has recently been reported,[4] in accord with Thorpe's[5] subsequent prediction that for real systems with van der Waals interactions between unbonded neighbors, the rigidity-percolation phenomena would be smeared out. With an interest in checking this prediction, and also in testing our suspicion that the vector-percolation concept might be more sensitively investigated in the *liquid* state of this system, we have extended the original study not only in composition range but also in temperature and variety of properties investigated. In particular, we have now included measurements of (i) the glass transition temperature T_g, (ii) changes in thermodynamic properties (expansivity α and heat capacity C_p) at T_g, and (iii) viscosity (the key liquid-state property) with striking results.

Most of the measurements reported will concern the pseudobinary join $Se_{(1-x)}(As_{0.5}Ge_{0.5})_x$, chosen by us to maximize the likelihood of random bonding, and hence conformity to mean-field arguments. In this study, our original sample preparation techniques have been refined in order to eliminate the oxygen contamination which vitiated the earlier results. High-purity lump elements (99.9999%) were melted together in evacuated silica tubes at 600–1150 °C, depending upon composition, for 24 h. They were then cooled at ~15 K/min. Prior to loading the tubes, the arsenic was placed in an evacuated chamber, the bottom of which was heated to 350 °C while the top was kept at 25 °C. This distilled off arsenic oxide contamination. The resulting samples, 65 in all, contained 100- to 200-ppm oxygen as determined by infrared spectroscopy.[6] They exhibited no evidence of crystallization in differential-scanning-calorimeter (DSC) thermograms.

Elastic constants were determined from sound-velocity measurements as described before,[3] but with an improved precision of 0.1%. Thermal-expansivity (α) measurements were made using a Perkin-Elmer model TMS-2, scanning at 2.5 K/min. The same instrument was used, with a beam-bending attachment, to determine the viscosity in the range 10^9–10^{13} Pa s with a precision *and* accuracy of ±5% (based on measurements made on BS710 standard glass). Heat-capacity C_p and enthalpy-relaxation measurements were made using the Perkin-Elmer DSC-4 differential scanning calorimeter at scan rates between 2.5 and 40 K/min.

The absence of universal or dramatic behavior of the longitudinal mechanical modulus C_{11} as the mean-field percolation threshold is crossed[4] is confirmed in this work for all $Se_{(1-x)}(Ge_yAs_{1-y})_x$ cuts across the ternary system. The results are more definitive than in binary systems[4] because of the extended $\langle r\rangle$ range available. In the As-Se binary and in Ge-poor glasses, we even observe[7] a contradictory maximum in C_{11} at or near $\langle r\rangle = 2.4$. Clearly the study of C_{11} at ambient temperature is not fruitful in the present context.

Turning to T_g (defined as the onset of the rises in C_p or α, as ergodicity is restored during heating at 20 K/min [see Fig. 1, inset (b)]), we observe more promising phe-

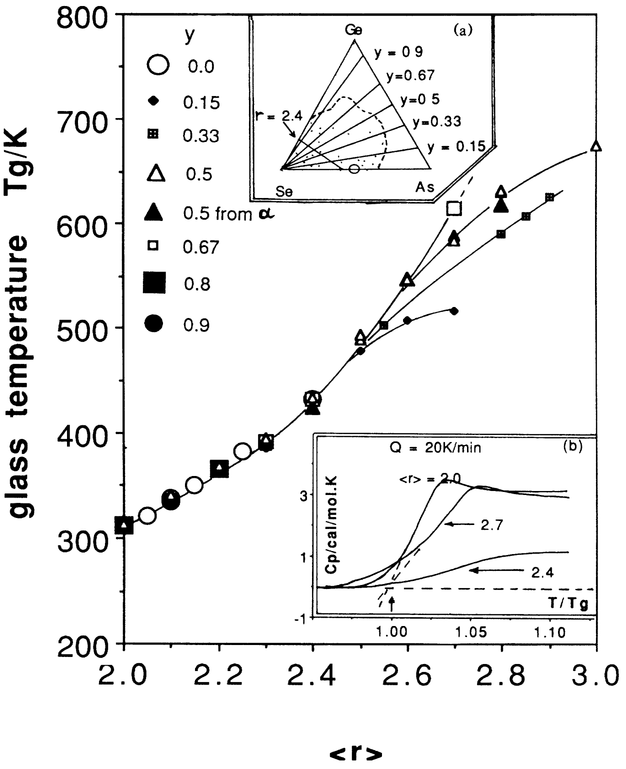


FIG. 1. $\langle r \rangle$ dependence of T_g from DSC and α, for Ge-As-Se glasses along various pseudobinary cuts $\mathrm{Se}_{(1-x)}(\mathrm{Ge}_y\mathrm{Se}_{1-y})_x$ as indicated in inset (a). Inset (b) shows behavior of the heat capacity C_p through the glass transition for $\langle r \rangle$ values at, and on either side of, the rigidity-percolation threshold along the $y=0.5$ join.

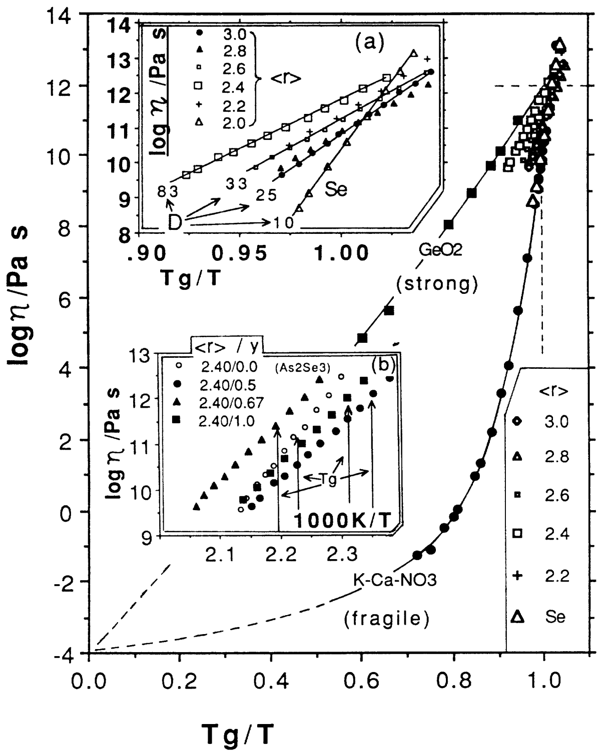


FIG. 2. Comparison of viscosities of pseudobinary ($y=0.5$) Ge-As-Se liquids near T_g, with the "strong" ($\mathrm{GeO_2}$) and "fragile" $[2\mathrm{Ca(NO_3)_2}\cdot 3\mathrm{KNO_3}]$ extremes of the liquid pattern (Ref. 8) from literature data, using a T_g-scaled Arrhenius plot. Inset (a) shows present results in more detail (note strong behavior at $\langle r \rangle = 2.4$). Equation (2) D values marked on plots are based on measured slopes (Arrhenius: $D=\infty$, slope$=16$). Inset (b) shows how strength is maintained at other $\langle r \rangle = 2.4$ points in ternary systems ($\mathrm{As_2Se_3}$ is exceptional, see text).

nomena. Figure 1 shows that T_g is a universal function of $\langle r \rangle$ up to and somewhat beyond the percolation threshold. It is only above $\langle r \rangle = 2.5$ that composition-specific effects enter, as different ways of disposing of the superfluous bonds are explored. There is, however, no sudden upturn in the $\langle r \rangle$ dependence of T_g to signal a threshold crossing. On the other hand, note the contrast in shapes of the heat-capacity scans at the threshold $\langle r \rangle$ value, and on either side of it: The heat-capacity "jump" at T_g in the vicinity of $\langle r \rangle = 2.4$ is so small and smeared out that we at first believed the sample had crystallized.

A small heat-capacity jump at T_g implies a strong resistance to structural degradation in the liquid state, and has been correlated with a minimum "fragility" (i.e., departure from Arrhenius viscosity behavior) in the overall pattern of viscous-liquid behavior.[8] (Fragility is a term being used[8-11] to characterize and quantify the anomalous non-Arrhenius transport behavior which develops in most glass-forming liquids as they approach the ergodicity-breaking[11] glass transition.) This interesting possibility stimulates three related questions to which we provide answers in Figs. 2 and 3. The first is, of course, whether the viscosity indeed passes through a fragility minimum at $\langle r \rangle = 2.4$, as implied by Fig. 1, inset (b). The second is whether this is also evidenced in a comparable minimum in the fragility behavior of the more fundamental enthalpy-relaxation time, τ_H (the time scale on which the system relaxes towards the state of zero excess entropy at T_K, the Kauzmann[12] temperature), and the third is whether or not the volumetric behavior through T_g, i.e., $\Delta\alpha$, will mimic the heat-capacity changes, ΔC_p. If $\Delta\alpha/\Delta C_p$ at the glass transition is *not* constant for all $\langle r \rangle$, then this system may also provide a test case for distinguishing between "free volume" and "entropy" theories for liquid relaxation processes.[13-15]

The inset (a) in Fig. 2 represents viscosity data on five of twelve compositions studied along the join $\mathrm{Se}_{(1-x)}(\mathrm{As}_{0.5}\mathrm{Ge}_{0.5})_x$, plotted in scaled Arrhenius form where the scaling temperature is the calorimetric T_g of Fig. 1. Within the error of the measurements, the results can be represented by straight lines in apparent conformity with the Arrhenius law but with wide variations in

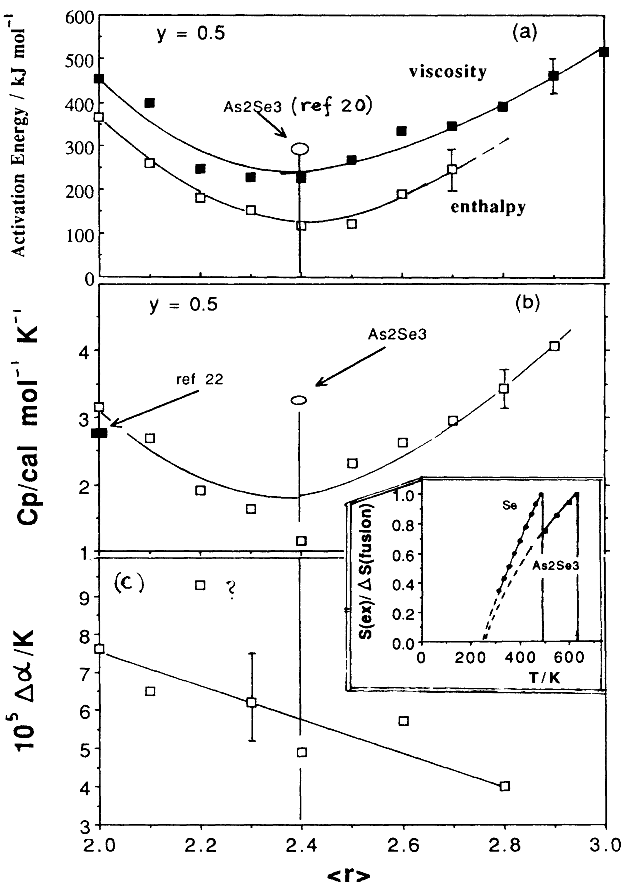
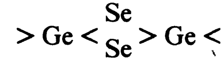


FIG. 3. $\langle r\rangle$ dependence of key relaxational and thermodynamic properties of $Se_{(1-x)}(Ge_yAs_{1-y})_x$ liquids at $y=0$ and 0.5: (a) Dependence of activation energies for viscosity and enthalpy relaxation. (b) Excess heat capacity ΔC_p measured at T_g showing minima in each case at the rigidity-percolation threshold $\langle r\rangle=2.4$. (c) Excess expansion coefficient $\Delta\alpha$ showing *absence* of anomaly at $\langle r\rangle=2.4$. Inset: Kauzmann plots for excess entropy in the cases $\langle r\rangle=2.0$ (pure Se) and $\langle r\rangle=2.4$ (pure As_2Se_3). Note how T_g/T_K differs according to liquid "strength." The values of T_g/T_K are predictable from Eq. (2) using D values based on the position of liquid in the strong-fragile classification.

viscosity preexponent as well as activation energy. However, when the same data are presented on the larger scale of T_g/T and compared with literature data covering a wider range of viscosities and temperature dependences, it can be seen that the present results simply represent the high-viscosity end of the same pattern of liquid behavior which has provided the basis for the "strong" and "fragile" liquids classification for which theoretical interpretations are currently being sought.[9,10,16] The remarkable thing is that compositions along a *single* pseudobinary cut in the present system cover almost the whole spectrum from strong to fragile behavior previously mapped out by combinations of data from many different liquid systems studied in a very wide range of temperatures.[8]

Of special interest in Fig. 2, of course, is the fact that the minimum fragility (minimum Arrhenius slope at $T_g/T=1$) observed in the present study occurs not at the highest value of $\langle r\rangle$ but rather at $\langle r\rangle=2.4$, the rigidity-percolation threshold. Evidently at higher $\langle r\rangle$ values, specific chemical effects such as the occurrence of double Se bridges



$$>Ge<\overset{Se}{\underset{Se}{}}>Ge<$$

[known to occur in pure $GeSe_2$ (Ref. 17)] enter into consideration. These are fragile structural elements.[18]

The inset (b) in Fig. 2 shows that the same low fragility is obtained for other ternary compositions with $\langle r\rangle=2.4$, lending credibility to the idea[1,2] of constraint counting involving *both* bond distances and angles[11,19] in these systems. The binary glass of $\langle r\rangle=2.4$, As_2Se_3 is, however, atypical according to Fig. 2, inset (b), having a more fragile character. It also has a larger enthalpy-relaxation activation energy, E_H (Ref. 20), and larger ΔC_p (Ref. 20) (see below). This is probably associated with its topological reorganization to give "raft"-like structures[21] of two-dimensional aspect.

Concerning our second question, the minimum in the "activation energy" seen at $\langle r\rangle=2.4$ for viscosity data is indeed also seen in the enthalpy-relaxation phenomena which determines the form of the heat-capacity scan. Using Moynihan's method of scan-rate-dependent T_g,[20] we obtain $E_H=Rd(\ln Q)/d(T^{-1})$, where Q is the scan rate. This quantity, for each of the glasses for which viscosity data were presented in Fig. 2, is plotted together with the viscosity activation energy E_η in Fig. 3(a). The minimum at $\langle r\rangle=2.4$ is even better defined for E_H, though the experimental precision of E_H is smaller.

We now return to the initial observation of Fig. 2 that the heat-capacity jump at T_g, ΔC_p, is remarkably small at $\langle r\rangle=2.4$ compared with the values at higher and lower $\langle r\rangle$. Figure 3(b) shows this quantity, obtained semiquantitatively ($\pm 10\%$), as a function $\langle r\rangle$ for all the $x=0.5$ glasses, together with a value for pure Se from Ref. 22. The correlation of a minimum in fragility with a minimum in ΔC_p is to be expected from the Adam-Gibbs equation,[14]

$$\eta=\eta_0\exp(C/TS_c). \qquad (1)$$

This is because, when ΔC_p is very small, S_c [$S_c=\int_{T_K}^{T}(\Delta C_p/T)dT$, where T_K is the Kauzmann liquid-crystal isoentropy temperature[11]] is almost temperature independent and Eq. (1) becomes equivalent to the Arrhenius law with the strong-liquid preexponent. The great differences in departures from Arrhenius behavior seen in Fig. 2 then suggest that a further (and very important) correlation be sought, as follows.

The pattern of viscosity behavior leading to the strong- and fragile-liquid classification can be reproduced by a modification, Eq. (2), of the famous Vogel-Tammann-Fulcher (VTF) equation in which the VTF B parameter is replaced by DT_0,

$$\eta = \eta_0 \exp[DT_0/(T-T_0)] . \quad (2)$$

The "strength" of the liquid goes as the parameter D in Eq. (2). This equation [which is easily derived from Eq. (1) when $\Delta C_p = K/T$ (Ref. 15)] requires that T_g lie far above T_0 for strong liquids whereas for highly fragile liquids T_g/T_0 approaches unity.[8,9] From Fig. 3, therefore, we would predict that T_K ($\equiv T_0$) values for fragile Se and stronger As_2Se_3 ($\langle r\rangle = 2.4$) will be much more similar than are their T_g values (307 and 455 K, respectively). Since these are both congruently melting compounds, T_K can be assessed by the purely thermodynamic route described by Kauzmann.[12] The data necessary to check this expectation are available.[22,23] We obtain for Se, $T_K = 240 \pm 10$ K.[22] This is demonstrated by the Kauzmann plot, inset to Fig. 3. The value of T_K for As_2Se_3 is found to be 236 ± 10 K (Ref. 22) (As_2S_3, $T_K = 265$ K), also demonstrated in the inset to Fig. 3. Thus our expectation is confirmed, though the near identity of T_K values was unexpected. It is reminiscent of the behavior of systems such as $ZnCl_2$-KCl and SiO_2-Na_2O in which the T_0 of Eq. (2) is invariant during network breaking.[24]

Using these results, we find that T_g/T_K values for these two compositions are 1.23 and 1.90. From Eq. (2), these values go with D values of 8.5 and 33, which may be compared with the observed extremes for all liquids of 3.5 and ~100.[9,25] The slopes of the scaled Arrhenius plots at T_g, given by $(DT_K/2.3T_g)(1-T_K/T_g)^{-2}$, are predicted from the T_g/T_K values to be 85.9 and 33.7. These are in good agreement with the values observed in Fig. 2 (76.6 and 34.3)—perhaps fortuitously so considering the extrapolations (to get T_K) and approximations [to get Eq. (2) from Eq. (1)].

Thus, on a semiquantitative level, we have correlated the bond connectivity in the model covalent *liquid* system Ge-As-Se with two of the key viscous-liquid experimental observations, viz., strong-to-fragile (variably non-Arrhenius) transport behavior, and the Kauzmann vanishing-excess-entropy conundrum. It remains to examine systematically the relation to $\langle r\rangle$ of the *nonexponentiality* of relaxation described by the Kohlrausch function $\exp(-[t/\tau_0]^\beta)$,[26] and of the *nonlinearity* of the various relaxation processes.[27] Here we note that a T_K value identical with ours has been obtained by Hodge[28] from an Adam-Gibbs-based analysis of nonlinear enthalpy relaxation. This is the subject of continuing investigation. We expect the technologically important low-loss characteristics of these glasses at $\langle r\rangle > 2.4$ (Ref. 29) will find a natural explanation in terms of the removal of "floppy" modes.[2]

We will discuss elsewhere how the finding $\Delta\alpha/\Delta C_p \neq$const for $\langle r\rangle > 2.4$ seen in Fig. 3(c) (i.e., the answer to our third question) favors entropy-based, over free-volume-based, interpretations of viscous-liquid transport and relaxation data.[13-15]

This work has been supported by the Office of Naval Research under Contract No. N00014-87-K-0471 and N0014-84-K-0289.

---

[1] J. C. Phillips, J. Non-Cryst. Solids **34**, 153 (1979).

[2] M. F. Thorpe, J. Non-Cryst. Solids **57**, 355 (1983); J. C. Phillips and M. F. Thorpe, Solid State Commun. **53**, 699 (1985).

[3] B. L. Halfpap and S. M. Lindsay, Phys. Rev. Lett. **57**, 847 (1986).

[4] S. S. Yun, Hui Li, R. L. Cappelletti, R. N. Enzweiler, and P. Boolchand, Phys. Rev. B **39**, 8702 (1989); B. Swiler and A. Varshneya, in Proceedings of the American Ceramic Society 1989 Fall Meeting, Glass Division (American Chemical Society, Washington, DC, to be published), Abstract No. 31-G-89F.

[5] M. F. Thorpe (private communication); H. He and M. F. Thorpe, Phys. Rev. Lett. **54**, 2107 (1985).

[6] D. S. Ma, P. S. Danielson, and C. T. Moynihan, J. Non-Cryst. Solids **37**, 181 (1980).

[7] B. L. Halfpap and S. M. Lindsay (to be published).

[8] C. A. Angell, J. Non-Cryst. Solids **73**, 1 (1985).

[9] J. Setthna, Europhys. Lett. **6**, 529 (1988).

[10] F. H. Stillinger, J. Chem. Phys. **88**, 7818 (1988).

[11] D. Stein and R. Palmer, in *Complex Systems*, Santa Fe Institute Studies in the Science of Complexity, edited by D. Stein (Addison-Wesley, Reading, MA, 1989), p. 759.

[12] W. Kauzmann, Chem. Rev. **43**, 219 (1948).

[13] M. H. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 (1959); M. H. Cohen and G. S. Grest, Phys. Rev. B **20**, 1077 (1979).

[14] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).

[15] C. A. Angell and W. Sichina, Ann. N.Y. Acad. Sci. **279**, 53 (1976).

[16] G. Frederickson, Ann. Rev. Phys. Chem. **39**, 149 (1988); K. L. Ngai, J. Non-Cryst. Solids **95&96**, 969 (1987).

[17] A. C. Wright (private communication).

[18] C. A. Angell and C. C. Phifer, Mater. Sci. Forum **32-33**, 373 (1988).

[19] P. Boolchand, J. Grothaus, and J. C. Phillips, Solid State Commun. **45**, 183 (1983); J. C. Phillips, Solid State Commun. **47**, 203 (1983).

[20] C. T. Moynihan, A. J. Easteal, J. Wilder, and J. C. Tucker, J. Phys. Chem. **78**, 2673 (1974).

[21] P. Boolchand, W. J. Bresser, and P. Suranyi, Hyperfine Interact. **27**, 385 (1986).

[22] S. S. Chang and A. B. Bestul, J. Chem. Thermodyn. **6**, 325 (1974); S. S. Chang (private communication).

[23] M. B. Myers and E. J. Felty, J. Electrochem. Soc. **117**, 818 (1970); A. J. Easteal, J. Wilder, R. K. Mohr, and C. T. Moynihan, J. Am. Ceram. Soc. **60**, 134 (1977).

[24] C. A. Angell, J. Am. Ceram. Soc. **51**, 124 (1968); A. J. Easteal and C. A. Angell, J. Phys. Chem. **74**, 3987 (1970).

[25] C. A. Angell, J. Phys. Chem. Solids **49**, 863 (1988).

[26] M. Shlesinger, Ann. Rev. Phys. Chem. **39**, 269 (1988).

[27] C. T. Moynihan *et al.*, Ann. N.Y. Acad. Sci. **279**, 15 (1976).

[28] I. M. Hodge (private communication).

[29] J. T. Krause, C. R. Kurkjian, D. A. Pinnow, and E. A. Sigerty, Appl. Phys. Lett. **17**, 367 (1970).