

NATURE OF GLASS TRANSITION IN CHALCOGENIDES

dedicated to Stanford R. Ovshinsky on the occasion of his 80th anniversary

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Glass transition endotherms in the *floppy*, *intermediate* and *stressed rigid* phases of chalcogenide glasses are examined by modulated DSC. In general, the T_g endotherms consist of *two* parts; a *reversing heat flow* that represents the configurational energy difference between glassy- and liquid- state, and a *non-reversing heat flow* that represents relaxation enthalpy of a glass. Experiments reveal that the *reversing heat flow in all the three phases does not age*, reflecting the ergodic fraction of heat flow. On the other hand, the *non-reversing heat flow steadily ages* (at $T < T_g$) to saturate in both the *floppy* and *stressed rigid* phases. For glasses in intermediate phases, *non-reversing heat flow* term is found not only to nearly *vanish*, but also *not to age*. Glasses in the intermediate phase are, indeed, quite special; they possess stress-free backbones, glass transitions that are almost completely thermally reversing, and do not age.

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1. Introduction

The glassy state of matter is ubiquitous. It is generally held that the majority of water in the universe is glassy in nature. Lightning strikes on sandy beaches or deserts from time immemorial have produced in instances over foot long columns of molten sand known as Fulgurites [1], God's own silica glasses. On the other hand, man made optical fibers from refined sand (silica), and rewritable optical disks [2] based on chalcogenides constitute now some of the most widely used glassy materials in present day communication and information technologies. Glasses are thus some of the oldest, and also some of the newest materials. Stanford Ovshinsky amongst other things has pioneered [2] the rewritable optical recording disk, which is now manufactured by Matsushita. On this special occasion of Stan's 80th birthday, it is, indeed, a great pleasure to dedicate this article to him. One of us (PB), owes a special word of thanks to Stanford Ovshinsky and to John P. deNeufville [3,4] for their collaboration and support in the early phase of work on chalcogenide glasses and thin-films.

A glass upon heating softens at a characteristic temperature, known as the glass transition temperature, T_g , when molar volumes (V) and enthalpy (H) undergo a qualitative change [5] as schematically shown in Fig. 1. The temperature derivatives of these quantities i.e., thermal expansion and specific heat, also change measurably and are used to detect the glass transition. Furthermore, structural relaxation times $\tau(T)$ as reflected in viscosity, also change qualitatively [6] by several orders of magnitude from the glassy state ($T < T_g$) to the liquidus ($T > T_l$). In spite of these remarkable

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signatures, the nature of the glass transition continues to pose formidable challenges. In 1995, P.W. Anderson captured [7] the prevailing spirit when he remarked that, "the deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition; this could be the next breakthrough in the coming decade..."

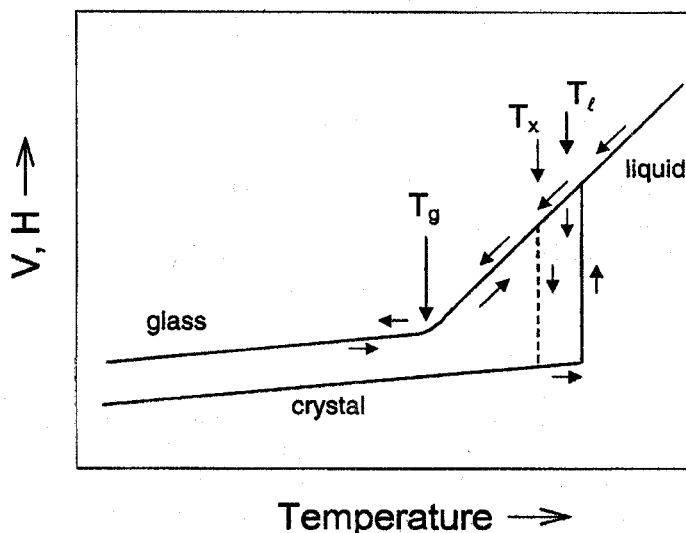


Fig. 1. Schematic T-variation in molar volumes (V) and enthalpy (H) of a glass forming liquid as it is supercooled to bypass crystallization, and show a second order transition near T_g , the glass transition temperature. Upon heating a glass past T_g , crystallization could occur at T_x and the crystal would melt at the liquidus T_l . Upon very slow-cooling, the liquid could also undergo a first order crystallization at T_c .

In the past five years important strides to understand elastic phase transitions in glasses have been made. A structure-based approach to the elastic thresholds has resulted in a *floppy-intermediate-stressed rigid* classification [8-11] of network glasses. *Intermediate phases* consist of optimally constrained ($n_c = 3$) backbones that open in between mechanically *floppy* (under constrained, $n_c < 3$) and *stressed rigid* (over constrained, $n_c > 3$) ones. Here n_c denotes the count of Lagrangian bonding constraints per atom. These constraints are due to bond-stretching and bond-bending forces, and the optimal value [8] of 3 derives from the atomic degrees of freedom associated with a 3d network.

These new developments are beginning to have an impact in fields far removed from glass science, and some of these include protein-folding and high temperature superconductivity. Proteins fold in *transition states* that separate the *denatured-* from the *folded-* state, and there are growing indications that the *transition states* actually form part of an *intermediate phase*, as suggested by the work of M. F. Thorpe [12]. The constraint counting algorithms elegantly show that the similarity between *biological and glassy networks* is far more quantitative than hitherto recognized. High Temperature Superconducting phases are known to open near a metal-insulator transition at an optimal doping of carriers in a base-insulating phase. Carriers in these stress-prone oxides are viewed to be part of disordered phases (electronic glasses) that apparently self-organize opening superconducting phases in between base-insulating and over-doped Fermi liquid phases, as suggested by J. C. Phillips [13]. The challenge to understand these complex materials and the underlying phase transitions is that they form part of *intermediate phases* [13] that are *non-mean-field phases* generic to disordered systems.

In this review we discuss the nature of glass transitions in the *floppy*, *intermediate* and *stressed rigid* phases. In general, we find glass transitions in *intermediate phases* to be almost completely *thermally reversing* in character, while in both *floppy* and *stressed rigid* phases to possess a substantial *thermally non-reversing character*. We have now performed aging experiments and find, in general, that the *reversing heat flow signal* does not age. On the other hand, the *non-reversing heat*

flow signal ages in both the floppy and stressed rigid phases, but not in intermediate phases. Some of the broad consequences of these new results on the nature of the glass transition are commented upon.

2. Glass transition temperature measurements

2.1 Differential scanning calorimetry (DSC)

Over the past 30 years, glass transition temperatures, T_g , have routinely been measured by DSC [14-16]. In the method, tens of milligrams of a glass sample of interest contained in an Al pan, is heated at a pre-determined scan rate of typically, $dT/dt = 10^\circ\text{C}/\text{min}$, and the heat flow to a sample (dH_t/dt) compared to that of an empty reference Al pan. Upon softening of a glass, an endotherm manifests at a threshold temperature as illustrated in Fig. 2a for the case of a relaxed GeS_2 glass sample. And the total heat flow rate is given by

$$dH_t/dt = C_p^{\text{kin}} dT/dt \quad (1)$$

wherein C_p^{kin} represents the kinetic specific heat of the glass sample. The kinetic specific heat has contributions both from configurational (change in state) and relaxation enthalpy (thermal history) of glasses. Furthermore in the process of measurement, because of the use of a finite scan rate, the endothermic event is in general up-shifted in T underscoring the kinetic nature of the transition. One can minimize these shifts by using a smaller scan rate ($dT/dt = 3^\circ\text{C}/\text{min}$ rather than $10^\circ\text{C}/\text{min}$), but such a change also reduces by 3-folds the signal size (dH_t/dt) that needs to be measured as shown by equation (1). For example, Fig 2b shows an MDSC scan of a GeS_2 glass [17] sample taken at $3^\circ\text{C}/\text{min}$. The total heat flow in this scan would be the same as performed in a DSC measurement. Note that the T_g (mid point) of 502°C obtained at $10^\circ\text{C}/\text{min}$ (Fig. 2a), has shifted down to 489°C at $3^\circ\text{C}/\text{min}$. (Fig. 2b), and the total heat flow signal has also reduced 3-folds.

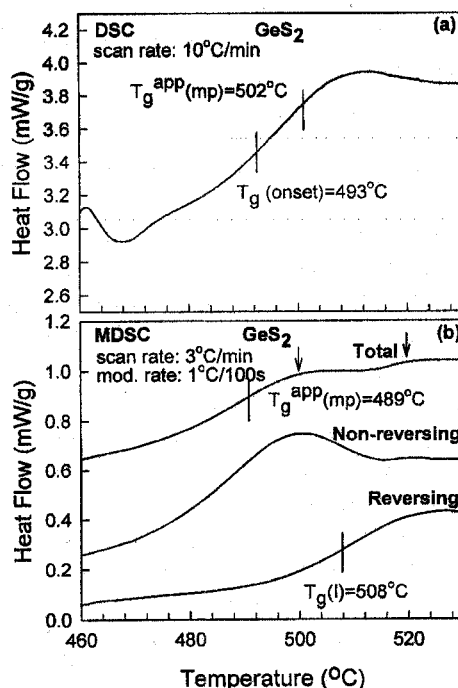


Fig. 2. (a) DSC scan of GeS_2 glass taken at $10^\circ\text{C}/\text{min}$ showing a T_g (mid point) of 502°C . (b) shows MDSC scan of a similar glass sample taken at $3^\circ\text{C}/\text{min}$ scan rate, and $1^\circ\text{C}/100\text{s}$ modulation rate, illustrating the total, non-reversing and reversing heat flow signals. The total heat flow rate would be the same as observed in a DSC scan taken at $3^\circ\text{C}/\text{min}$. Note that the apparent T_g has shifted down to 489°C upon reducing the scan rate. The T_g (inflexion) inferred from the reversing heat flow is 508°C . Fig. is taken from ref. 17.

2.2 Temperature modulated differential scanning calorimetry (MDSC)

A new variant of DSC, called Temperature Modulated DSC, was introduced about seven years ago. In such an instrument [18-22], as for example the model 2920 from TA Instruments Inc., a sinusoidal temperature ($T_m \sin \omega t$) profile is superposed onto a fixed ramp (dT/dt) in programming a scan. This has the consequence that one can now deconvolute the total heat flow (dH_t/dt) into a part that tracks the T- modulations, called the *reversing heat flow* (dH_r/dt), and the remainder (dH_{nr}/dt) that does not track these modulations and is termed the *non-reversing* heat flow, as is illustrated by equation (2a):

$$dH_t/dt = dH_r/dt + dH_{nr}/dt \quad (2a)$$

$$dH_t/dt = C_p dT/dt + dH_{nr}/dt \quad (2b)$$

In equation (2b), C_p represents the thermodynamic specific heat. The separation of the total heat flow into a *reversing* or *ergodic* fraction and a *non-reversing* or *non-ergodic* fraction has broad consequences. But before we get into these, it may be useful to emphasize upfront that in use of MDSC, certain stringent operating conditions must be met for the deconvolution that involves a Fourier transform of the modulated heat flow signal to yield reliable results as discussed elsewhere [18]. Furthermore, the modulation frequency in general cannot usually exceed 0.03 Hz, to permit good heat transfer to the sample, and also a steady state heat flow to occur in usual glass samples of interest.

Some recent MDSC studies have been performed in Fourier space [21,22] where the quantity of interest is a frequency dependent specific heat that is extracted from the linear response (sinusoidal) of the sample enthalpy. It appears that the analysis of the heat flow in Fourier space through complex heat capacity has permitted to extend to lower frequencies ω (up to 0.01 Hz) previous AC calorimetric studies of Birge and Nagel [24]. The non-reversing heat flow term has permitted establishing very simply the relaxation time of a glass-forming liquid with temperature, which is in agreement with dielectric measurements [25]. It provides a precise measure of the Kohlrausch-Williams-Watt stretched exponent β [26] in several some organic glass formers.

Fig. 2b shows a scan of a GeS_2 glass sample but this time studied in the MDSC mode. Here we observe the *non-reversing heat* flow signal to show a broad but asymmetric peak, as a precursor to the *reversing heat* flow signal. The latter signal shows a characteristic step that we normally associate with a glass transition, and its inflexion point (or mid point) can be used to define a T_g . In these experiments the *reversing heat* flow signal always sits on a flat baseline [18,19] irrespective of the equipment baseline. Furthermore by scanning up in T and then scanning down in T, and taking the average, i.e., $\frac{1}{2}\{T_g(\text{up}) + T_g(\text{down})\}$, one obtains a *scan rate independent* [18,19] T_g .

The area under the *non-reversing heat* flow peak serves to define the *non-reversing heat*, ΔH_{nr} , [20] associated with the glass transition. In many DSC measurements the overshoot of the endotherm encountered in aged samples is actually a manifestation of the ΔH_{nr} signal, and it is particularly pronounced in under-coordinated glasses such as Se [27]. The peak in dH_{nr}/dt signal is usually asymmetric, and in over-coordinated glasses such as GeS_2 it usually has a high-T tail. The presence of this tail can reduce the jump in C_p across the glass transition, i.e., $\Delta C_p = C_p^{\text{liq}} - C_p^{\text{gl}}$, that one would infer simply by looking at the saturation values of the total heat flow in the glass- and in the liquid- state, as one normally does [1] in a DSC measurement.

A careful reader will also notice that in Fig. 2b, the total heat flow reveals a pair of peaks (see arrows). The first peak centered near 500 °C actually comes from the *non-reversing heat* flow signal, while the second peak centered at about 520 °C has contributions from the *reversing heat* flow signal that actually determines T_g . Strikingly parallel results are found in the companion GeSe_2 glass as discussed elsewhere [28].

We have examined several families of chalcogenide and chalcohalide glasses by modulated DSC [29]. Compositional trends in T_g in select systems are summarized in the next section, while those in ΔH_{nr} are presented in section 4.

3. Compositional trends in T_g in chalcogenide glasses

3.1. Stochastic limit (near $\bar{r} = 2$)

A small increase of a few degrees Celsius in T_g of a glass sample can be brought about by synthesis (quench rates) and/or by sub- T_g aging in a DSC measurement. But chemical alloying can bring about much larger changes in T_g of up to several hundreds of degrees Celsius. For example the T_g of a Se glass of 40 °C, can be increased [28] to about 400°C by alloying 33 mole percent of Ge, as in GeSe₂ glass (Fig. 3). In a parallel fashion, T_g of Se glass can also be increased to about 200 °C by alloying 40 mole% of As [26,20] as in As₂Se₃ glass (see Fig. 3). R. Kerner and M. Micoulaut [31] have developed a stochastic agglomeration theory to understand changes in T_g brought about by cross-linking of a Se_n-chain network by 3-fold coordinated As and/or 4-fold coordinated Ge. In these combinatorial calculations [32] specific local bonding configurations are thought to bond with each other in a stochastic fashion to grow a cluster, whose size is largely controlled by T and underlying bond strengths. Thus, for example, in Ge-Se glasses, Se-Se chain segments and Ge(Se_{1/2})₄ tetrahedra represent the local bonding configurations that polymerize in a stochastic fashion. Underlying chemical bond strengths (E_{Ge-Se} , E_{Se-Se}) control evolution of the network as T changes. As the T is lowered the polymerization process saturates and permits defining a glass transition temperature. For binary IV-VI glasses such as Ge_xSe_{1-x}, these calculations [32] reveal that the slope,

$$dT_g/dx = T_0/\ln 2 \quad (3)$$

and is *parameter free*. Here T_0 designates the glass transition of the base network, Se glass in our case. It is quite remarkable that variations in T_g with an additive depend neither on kinetic nor on viscoelastic parameters that are thought to control T_g . These predictions are in excellent accord with experiments at $x < 0.10$ in both the Ge-Se and Si-Se binary [28]. These results suggest that the increase of T_g is a measure of global connectivity of a glass network. Changes in T_g brought about by using a higher melt-quench rate or prolonged aging of a glass sample, can likewise be traced to atomic changes in the degree of polymerization or of connectivity of networks.

The role of chemical bond strengths in normalizing glass transition temperatures of networks possessing the same degree of connectivity or mean coordination number has also been recognized [33]. Analysis of T_g trends in corresponding sulfide-, selenide- and telluride- glasses reveals [34] that in so far as network connectivity is concerned, the number of ways in which local units can combine, i.e. entropy of mixing, apparently controls the slope dT_g/dx observed in these glasses. Bond strengths changes of 5 % or less play no role whatsoever in determining T_g . It is therefore not surprising that attempts to understand T_g trends based strictly on chemical bond strengths alone [35] run into difficulties [33]. Such purely chemical trends do not take into account aspects of structure (global connectivity) that apparently control variations in T_g .

3.2 Nanoscale phase separation limit (near the thresholds $\bar{r} = 2.40$ and 2.67)

A particularly striking feature of the compositional trends in $T_g(r)$ of Fig. 3, is the existence of a threshold behavior when \bar{r} increases to 2.40 in the As-Se binary, or to 2.67 in the Ge-Se binary. But no such thresholds are observed in the As-Ge-Se ternary containing *equal concentrations of As and Ge*, wherein T_g s are found to increase almost linearly with composition or mean coordination number \bar{r} . The behaviour is not unique to the As-Ge-Se ternary but is observed [33] in other ternaries, including the P-Ge-Se, As-Ge-S where complete results are now available.

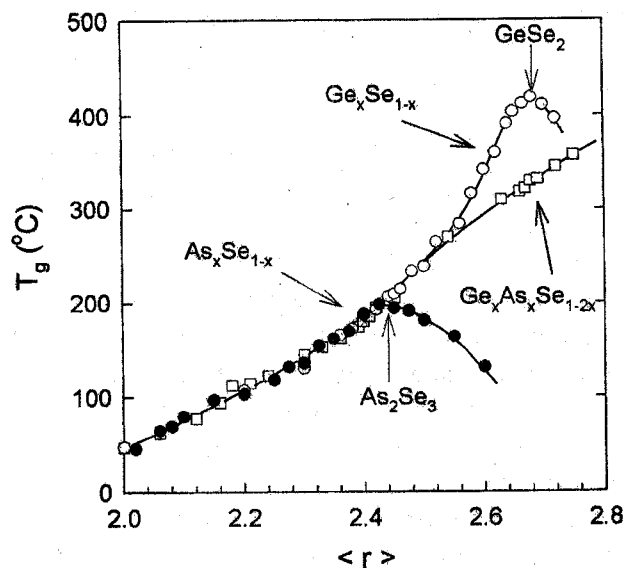


Fig. 3. Measured T_g s of indicated glasses plotted as a function of \bar{r} . T_g s are those measured from the reversing heat flow in MDSC measurements corrected for the finite scan rate of 3 °C/min. $\bar{r} = 2 + x$ for the As-Se binary, $\bar{r} = 2(1 + x)$ for the Ge-Se binary, and $\bar{r} = 2 + 3x$ for the As-Ge-Se ternary. Figure is taken from ref. 33.

We have suggested that these thresholds in T_g constitute evidence for *nanoscale phase separation* of molecular networks [33] once the cation concentrations exceed the chemical thresholds in the binary glasses. This is to say that Ge-Ge (As-As) bonds formed in binary Ge-Se(As-Se) glasses, do not form part of the backbone once the cation concentration exceeds the chemical threshold composition of $\bar{r} = 2.67$ (2.40). Thus those ideas based on stochastic agglomeration theory that permit us to understand an increase in T_g upon adding As or Ge in a Se glass, also permit one to understand, at least qualitatively, why T_g s decrease once \bar{r} exceeds the chemical thresholds. Indeed, substantial experimental evidence [17,29] for these *nanoscale phase separation effects* in binary glasses is now available from local probes (Mössbauer spectroscopy, Raman scattering) and inelastic neutron scattering [36] measurements.

In the Ge-As-Se ternary containing equal concentrations of As and Ge, the very special T_g behaviour [37] can be traced to suppression of nanoscale phase separation effects due in part to the presence of chemical disorder. In other words, equal concentrations of $\text{As}(\text{Se}_{1/2})_3$ pyramids and $\text{Ge}(\text{Se}_{1/2})_4$ tetrahedra in ternary $\text{As}_x\text{Ge}_x\text{Se}_{1-2x}$ glasses suppresses nucleation of binary nanocrystalline phases. The behaviour is observed in other ternaries but is not generic.

In a series of rather exhaustive DSC measurements, S. Mahadevan and A. Giridhar [38,39] established compositional variation of T_g in ternary $\text{Sb}_y\text{Ge}_x\text{Se}_{1-x-y}$ glasses at $0 < y < 0.10$ and $0 < x < 0.34$ range. They found that the *threshold behavior* (global maximum) in T_g near $x = 1/3$, at $y = 0$, systematically shifts to lower temperatures as y increases (see Fig. 4a). These results constitute evidence of *phase separation* of the Sb additive into an Sb_2Se_3 rich-nanophase that segregates from the base glass $\text{Ge}_t\text{Se}_{1-t}$ phase as discussed by us [33] recently. The plot of Fig. 4b compares the observed shifts (data points) in the threshold value of $T_g(y)$ with the predicted ones [33] based on such a model (continuous line). The sharply contrasting behaviour of Sb in relation to As as an additive in the Ge-Se base glasses is undoubtedly related to the more metallic and polarizable character of the heavier cation.

The underlying effect probably has the same physical origin as the one observed by Lucovsky et al. [40] in their experiments on zirconia or hafnia doped silica to produce what they have termed "*modified random networks*". Here the *modified phase* consists of the hafnia or zirconia nanophases that apparently segregate from the SiO_2 base glass. The base glass here, of course, represents the prototypical example of a self-organized oxide network, for reasons that are discussed elsewhere [41-43] in the literature.

4. Compositional trends in $\Delta H_{nr}(x)$ and thermally reversing windows

An advantage of the use of MDSC to examine glass transition endotherms is that one can *independently* track changes in the *reversing and non-reversing heat flow* signals, as a function of glass chemical compositions. Some of this information was already presented in section 3, where we discussed compositional trends in T_g deduced from the *reversing heat flow* signals. Of equal interest if not more is the *non-reversing heat flow* signal and particularly its variation as a function of glass composition. As mentioned earlier, these results reveal the existence of compositional windows across which the non-reversing heat, $\Delta H_{nr}(x)$, is found to nearly vanish [10]. These windows are denoted as *thermally reversing windows* [10].

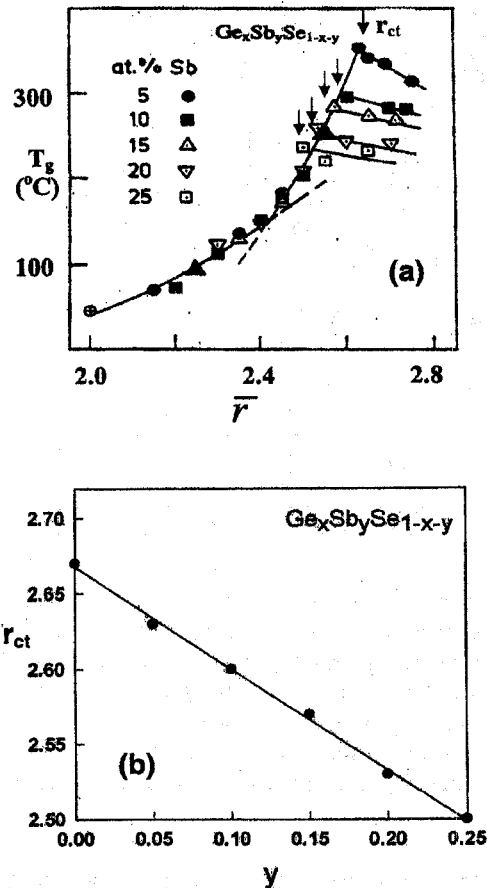


Fig. 4. (a) DSC inferred T_g s of titled ternary glasses at indicated Sb concentrations (y) taken from ref. 38 showing the threshold behaviour (arrow) in T_g to systematically shift to lower r as the Sb content increases. (b) shows a plot of the observed threshold mean coordination number, r_{ct} , change as a function of Sb content. The straight line is the prediction of a nanoscale phase separation model developed in ref. 33. The excellent agreement between the observation and prediction suggests that the Sb additive segregates into an Sb_2Se_3 nanophase in the Ge-Se base glass.

4.1. Si_xSe_{1-x}

Bulk glass samples in the $0.15 < x < 0.34$ composition range at 0.01 interval were examined in Raman scattering and MDSC measurements by Selvanathan et al. [44-45]. These glass samples are rather hygroscopic, and for that reason it was convenient to perform the Raman scattering measurements in the quartz tubes used to synthesize them. Particular care was exercised to thoroughly vacuum bake Al pans and lids prior to transferring the glass samples in the hermetically sealed pans in a dry nitrogen ambient (glove box) for the MDSC experiments. The glass samples were relaxed below

T_g for several weeks prior to the MDSC measurements. Fig. 5a displays compositional trends in $\Delta H_{nr}(x)$; one observes a sharp and deep reduction in the heat near $x_c(1) = 0.20$ or $\bar{r}_c(1) = 2(1+x) = 2.40$, followed by an equally sharp increase near $x_c(2) = 0.27$ or $\bar{r}_c(2) = 2.54$. These trends give rise to a square-well like pattern with the walls serving to define the extremities of the *thermally reversing window*. In the window, glass transition endotherms become almost completely *thermally reversing* in character.

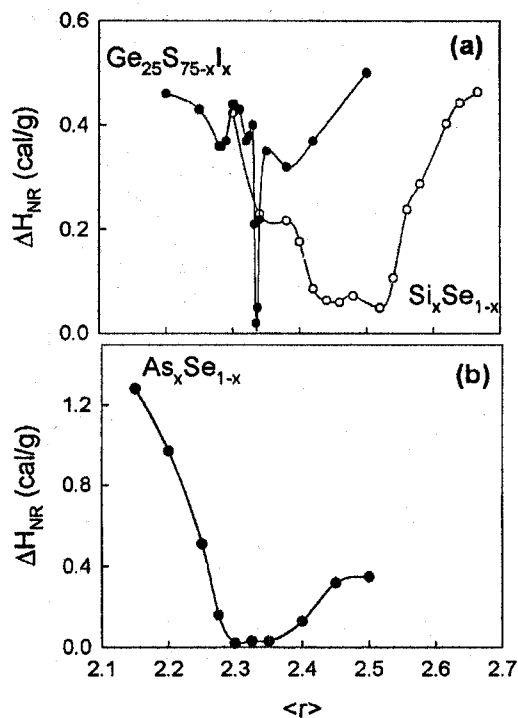


Fig. 5. The non-reversing heat, ΔH_{nr} , in (a) the Si-Se and the Ge-S-I ternary glasses taken from refs 44, and 49 respectively and (b) the As-Se binary glass system taken from ref. 20. Notice that the thermally reversing window in the Si-Se binary is shifted up while that in the As-Se shifted down in relation to the mean-field $r = 2.40$ value. The singularly narrow window in the Ge-S-I ternary illustrates the absence of self-organization. For the ternary, the centroid of the peak corresponds almost exactly to the mean field value of the floppy-rigid transition predicted by extended constraint theory as described in ref. 47.

Further confirmation for the existence of these thresholds was given in Raman scattering [44,45]. From the observed lineshapes, the frequency of corner-sharing $\text{Si}(\text{Se}_{1/2})_4$ tetrahedra ($v_{cs}(x)$) was established [45]. Compositional trends in $v_{cs}(x)$ reveal kinks (change in slope) near the two thermal thresholds ($x_c(1)$ and $x_c(2)$) indicated above. In fact the two elastic thresholds established from the Raman results more accurately establish the critical points than from the thermal ones inferred from MDSC. Glass compositions in the $x_c(1) < x < x_c(2)$ range represent the *intermediate phase*, those at $x < x_c(1)$ the *floppy phase*, while those at $x > x_c(2)$ the *stressed rigid phase* in this binary system [44,45]. The sharpness of the *intermediate phase* in this system is rather striking and is probably due to chain fragments of *isostatically rigid* edge sharing $\text{Si}(\text{Se}_{1/2})_4$ tetrahedra that define elements of medium-range-structure, used to estimate the width of the intermediate phase [46].

4.2. $\text{As}_x\text{Se}_{1-x}$

Compositional trends of $\Delta H_{nr}(x)$ in the titled binary taken from ref. [29] appear in Fig. 5b. One observes a *thermally reversing window* in the $0.28 < x < 0.38$ range corresponding to $2.28 < \bar{r} < 2.38$. This is a surprising result. The window appears at $\bar{r} < \bar{r}_c = 2.4$, the critical mean coordination number predicted by the mean-field description [8,9] for the onset of rigidity due to J. C. Phillips and M. F. Thorpe.

Compositional trend of $T_g(x)$ in these glasses at $x < 0.13$, show that the slope $dT_g/dx = 4.1$ °C/at.% As. This value of the slope is significantly lower than the predicted slope of

$$dT_g/dx = T_g / \ln(3/2) \quad (4)$$

of 7.7 °C/at.% As by stochastic agglomeration theory, if the only As centered local structures formed in these Se rich ($x < 2/5$) glasses consist of pyramidal $\text{As}(\text{Se}_{1/2})_3$ units.

Thus, trends in both $T_g(x)$ and $\Delta H_m(x)$ are *inconsistent* [20,30] with the prevailing view of molecular structure of these glasses as made up of Se_n chain fragments that are crosslinked by $\text{As}(\text{Se}_{1/2})_3$ units alone. These thermal results, on the other hand, as shown by Georgiev et al. [20], are *consistent* with the presence of both quasi-tetrahedrally coordinated $\text{Se} = \text{As}(\text{Se}_{1/2})_3$ units and pyramidally coordinated $\text{As}(\text{Se}_{1/2})_3$ units as the local building blocks of these Se-rich glasses. Both these local units are *isostatically rigid*, i.e. $n_c = 3$, as revealed by constraint counting algorithms with the difference that the mean coordination number, $\bar{r} = 2.28$ for the quasi-tetrahedral unit, but it equals 2.40 for the pyramidal units. And it is not a coincidence that these two values of \bar{r} actually correspond to the lower and upper limit of the thermally reversing window [20]. The inclusion of the quasi-tetrahedral units in the Stochastic agglomeration theory [20] lowers the slope dT_g/dx , and one can quantitatively also understand the reduction in slope if about 30% of the As units were quasi-four fold coordinated. The issue is currently the subject of EXAFS measurements.

4.3. $\text{Ge}_{0.25}\text{S}_{0.75-y}\text{I}_y$

In its original formulation [8,9], mean-field constraint theory was applied to describe networks containing atoms with a coordination number $\bar{r} \geq 2$. The theory was subsequently extended to include dangling ends or one-fold coordinated atoms [43,44], $\bar{r} = 1$. The choice of the present ternary permitted one to test the validity of these new ideas on constraints associated with dangling ends. In particular, the interest was to see if iodine for sulfur replacement would systematically lower the global connectivity of the marginally rigid base glass ($\text{Ge}_{0.25}\text{S}_{0.75}$), and lead to a *rigid to floppy* transition at a *critical* iodine concentration. These experiments [49] turned out to be far more revealing. Indeed, one did observe a reduction of T_g s, and a *rigid to floppy* transition at almost exactly the predicted composition, $y = y_c = 1/6$, of the iodine additive. But there was more, the results also showed [49] the transition to be unexpectedly sharp, as illustrated in the plot of Fig 5a, thus providing new insights into aspects of structure that apparently control the width of intermediate phases.

Why is the thermally reversing window in the iodine bearing ternary so narrow? The answer appears to be that rings, where rigidity nucleates [50], contribute to the width of the transition (or the thermally reversing window). In the ternary, the iodine for sulfur replacement almost *randomly* cuts these rings. The glass network is therefore unable to self-organize. At a local level, there are only two types of *isostatically rigid* units that comprise the stress-free backbone; $m = 1$ mixed tetrahedra, i.e. $\text{Ge}(\text{S}_{1/2})_3\text{I}_1$ and $m = 0$ units of the GeS_4 type that have S-S bridges. These local units apparently self-organize but only at a very special glass composition $y_c = 1/6$. Other local units ($m = 2, 3$ and 4) populated in the network are all under constrained [49] and rapidly lead to nanoscale phase separation of the floppy ($y > 1/6$) glasses.

The extremely narrow thermally reversing window in the iodine bearing ternary puts in perspective the much wider windows observed in the two binary glasses above. These results unambiguously show that substantial self-organization must be taking place in the two binary glasses in which a multitude of isostatically rigid local units contribute to the backbone.

5. Aging effects associated with the glass transition

In sharp contrast to crystalline solids, glassy networks, in general, are out of equilibrium and once formed will relax at $T < T_g$, i.e., age. Experimentally, this means that any physical property of a glass will depend on the waiting time t_w after it has been synthesized. Theoretically, aging is encoded in a two-time correlation function which is time translational invariant as long as one remains in the supercooled state [51]. In a glass, this invariance is not held any more, and the correlation function

depends on the waiting time t_w . Another consequence of the breakdown of the invariance is that the fluctuation dissipation theorem is violated in a glass. Aging properties have been extensively discussed in the case of lattice glasses [52] with orientational disorder (i.e. "spin glasses"), but conventional glasses, such as the one discussed above, have not received the same attention so far. To our knowledge, aging experiments on binary Ge-Se glasses have been performed only with DSC [53]. Within the context of MDSC measurements, aging raises the broader issue, in what manner do the two heat flow terms associated with the glass transition evolve as a function of time? In this section we address some of these issues.

Fig. 6 captures some of the salient results on binary As_xSe_{1-x} glasses. The intermediate phase [20] for this binary extends from $x = 0.28$ to $x = 0.38$ (see Fig. 2b). Three specific compositions in this binary were chosen to examine aging effects. These included, one at $x = 0.15$ in the *floppy phase*, one at $x = 0.30$ in the *intermediate phase*, and finally one at $x = 0.40$ in the marginally *stressed rigid* phase.

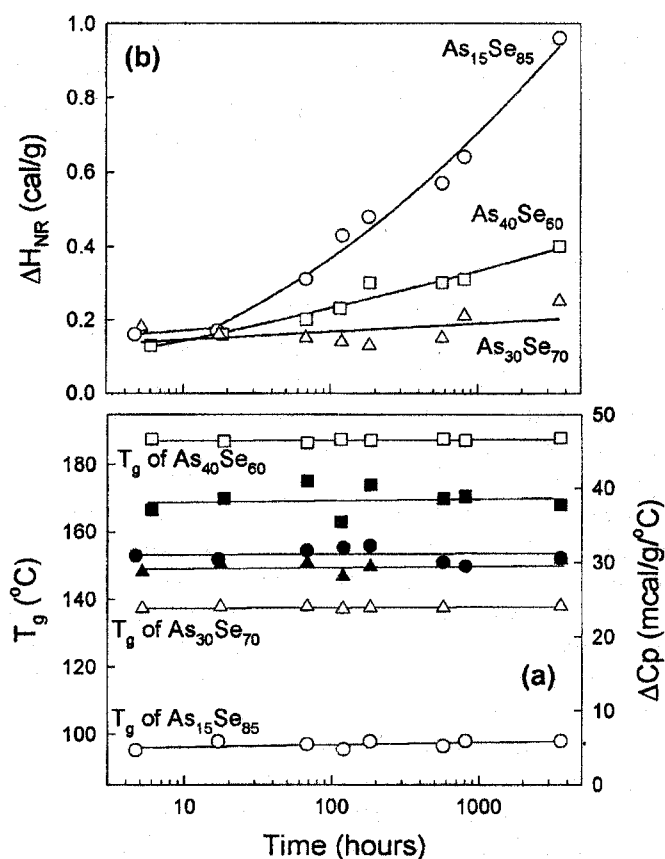


Fig. 6. Aging effects in (a) T_g (open symbols) and ΔC_p (filled symbols) deduced from the reversing heat flow and (b) the non-reversing heat, ΔH_{nr} , at $x = 0.15$ (floppy), 0.30 (intermediate), and 0.40 (stressed rigid) in As_xSe_{1-x} binary glasses. Note the absence of aging effects for the reversing heat flow related parameters in general, but the presence of it in the non-reversing heat flow signals for the floppy and stressed rigid compositions. The intermediate phase composition ($x = 0.30$) shows virtually no aging. See text for details.

5.1. The reversing heat flow and T_g

Bulk glass samples were aged at room temperature for extended periods and MDSC scans at a predetermined scan- and modulation- rates were undertaken. The heat capacity jump, ΔC_p , and the glass transition temperature, T_g , were deduced from the *reversing heat flow signal* the usual way. Fig. 6a provides a summary of the results. One finds neither T_g nor ΔC_p to show evidence of a change

over an aging period of 5 months for any of the three samples examined. Here the aging temperature (23 °C) is about 100 °C to 150 °C below T_g . These results lead us to believe that the *reversing heat flow* signal deduced from these MDSC scans apparently does not age for any of the glasses either in the *floppy*, or the *intermediate* or the *stressed rigid* phases. The only aging effect observed in the *reversing heat flow* signal is in the width of the glass transition ($\Delta T = T_g^{\text{onset}} - T_g^{\text{end}}$), which narrowed after 5 months of aging for the glass composition at $x = 0.15$ in the floppy phase. A parallel observation has been made in lightly doped Se glass [27]. No changes in the width of the glass transition were noted either for the $x = 0.30$ or the 0.40 glass composition.

5.2. The non-reversing heat flow

Fig. 6b provides a summary of aging effects observed on the *non-reversing heat*, ΔH_{nr} , for the three samples of interest. Here one can discern rather striking aging effects; the ΔH_{nr} term systematically increases by almost a factor of ten over a few weeks waiting time to eventually saturate for both the floppy ($x = 0.15$) and the marginally rigid ($x = 0.40$) glass compositions. But notice that for the glass composition in the intermediate phase ($x = 0.30$), the ΔH_{nr} term changes very little over an aging period of 20 weeks. Thus glasses in the intermediate phase not only have a vanishing ΔH_{nr} term, but the aging associated with that term is minuscule.

The aging behavior documented in Fig. 6 correlates well with the results on compositional trends of $\Delta H_{nr}(x)$ displayed in Fig. 5b. The latter results were obtained on samples that had aged for 2 weeks. Clearly if one had aged those samples longer (2 months for example), the thermally reversing window of Fig. 5b would actually be even deeper.

Several important insights have emerged from these aging experiments on the chalcogenides. The *reversing heat flow* signal in general *does not age*. Aging effects are almost entirely *localized* on the *non-reversing heat flow signal* and are pronounced in the *floppy* and *stressed rigid* phases. In sharp contrast, glasses in *Intermediate phases* not only possess a *vanishing non-reversing heat*, but that heat term remains vanishingly small and ages to a very small degree. It is clearly of interest to see if the present results extend to other network forming glass systems. In a recent paper, Carpentier et al. [22] have shown that in organic glass formers as well the reversing heat flow displays equilibrium behaviour. Our conclusions on the *floppy* and *stressed rigid* chalcogenide glasses would be representative of fragile glass-forming liquids.

5.3. On the nature of glass transition

Several questions emerge from the results above. Is the jump in the heat capacity at T_g from the *reversing heat flow signal*, a true phase transition? If so, what is the order of the transition? In the Ehrenfest classification, for a second order phase transition the Prigogine-Defay(PD) ratio [54] must equal 1. The PD ratio equals $[\Delta K \Delta C_p]/T_g V(\Delta\alpha)^2$ and depends on changes in the specific heat (ΔC_p), the thermal expansion ($\Delta\alpha$), and the bulk compressibility (ΔK) near T_g . Previous measures of the PD-ratio using kinetic ΔC_p^{kin} inferred from DSC measurements have placed the value [54,55] of this ratio typically in the 2-4 range in glass forming liquids. It is likely that the ΔC_p^{kin} inferred from these DSC measurements (of the total heat flow) overestimates the ΔC_p value. The latter can be inferred from the reversing heat-flow in MDSC measurements as discussed earlier in section 2. The latter ΔC_p values do not depend on either the glass sample history or the waiting time t_w , and furthermore could lead to smaller values of the PD ratio making the glass transition more nearly a second order transition. But before such a conclusion can be arrived at, reliable changes in ΔK and $\Delta\alpha$ near T_g would need to be established.

The configurational entropy associated with the glass transition is defined as

$$S_c(T) = \int_{T_K}^T \frac{C_p^{\text{kin}}(T)}{T} dT \quad (5)$$

where T_K is the Kauzmann temperature at which the configurational entropy vanishes. Since the total heat flow in an MDSC measurement can be separated between an ergodic and a non-ergodic

contribution, one could rewrite equation (5) using equation (2) to arrive at equation (6) below. In equation (6), the first term derives from the thermodynamic specific heat coming from the reversing heat flow, and the second term from the *non-reversing heat-flow*.

$$S_c(T) = \int_{T_K}^T \frac{C_p(T_i)}{T_i} dT_i + \int_{H_{nr}(T_K)}^{H_{nr}} \frac{dH_{nr}}{T} \quad (6)$$

It is the second term on the right that would determine changes in configurational entropy resulting from aging effects tied to thermal history. *Floppy* and *stressed rigid* glasses are expected to be *fragile*, while glasses in the *intermediate* phase to be *strong*. Thus chalcogen-rich glasses display characteristics of fragile behaviour, i.e. larger activation energies for T-dependence of viscosity [56] near T_g in contrast to glasses in the intermediate phase that display a smaller activation energy near T_g that is Arrhenius-like over wider temperature ranges.

Finally, we should stress that if a heterogeneous picture is assumed for the glass transition [57], then the jump in specific heat from the reversing heat flow and the peak in the non-reversing heat flow could be signatures of at least two relaxation time scales in the liquid, one being related to the heating rate q , the other to the modulation ω .

6. Concluding remarks

A structure-based approach has provided a means to understand elastic phase transitions in network glasses resulting in the *floppy-intermediate-stressed rigid* classification. Raman scattering measurements have provided the underlying elastic power-laws characterizing these phases. Thermal measurements using modulated DSC have shown the existence of *thermal thresholds* that coincide with the *elastic thresholds*. In particular, glass transitions for compositions in *intermediate phases* display vanishing *non-reversing heat flow* terms, giving rise to *thermally reversing windows*.

In the present work we have now investigated the role of aging on the glass transition endotherm. Measurements on binary As-Se glasses reveal that the *reversing heat flow signals* do not age either in the *floppy*, or the *intermediate*, or the *stressed rigid phase*. Aging effects appear to be entirely localized on the *non-reversing heat flow* term in the *floppy* and *stressed rigid* phases. In sharp contrast, glasses in *intermediate phases* possess not only a *vanishing non-reversing heat*, but that *heat term does not age* to any measurable degree.

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References

- [1] J. C. Zeitner, Fulgurites, Lapidary Journal, April 4, 1982. Also see <http://www.usfcam.usf.edu/McCollumPDF/0.4.Fulgurites.pdf>.
- [2] Stanford R. Ovshinsky in Insulating and Semiconducting Glasses, Ed. P. Boolchand, World Scientific Press, Inc., Singapore, 2000, p. 729.
- [3] W. J. Bresser, P. Boolchand, P. Suranyi, J. P. deNeufville, Phys. Rev. Lett. **46**, 1689 (1981).
- [4] P. Boolchand, B. B. Triplett, S. S. Hanna, J. P. deNeufville in Mössbauer Effect Methodology **9**, 53 (1974).
- [5] R. Zallen, The Physics of Amorphous Solids, J. Wiley & Sons, New York, 1983, p.2.
- [6] A. C. Angell in Insulating and Semiconducting Glasses, Ed. P. Boolchand, World Scientific Press, Inc., Singapore, 2000, p.1.

- [7] P. W. Anderson, *Science* **267**, 1615 (1995).
- [8] J. C. Phillips, *J. Non-Cryst. Solids* **34**, 153 (1979).
- [9] M. F. Thorpe, *J. Non-Cryst. Solids* **57**, 355 (1983).
- [10] P. Boolchand, D. G. Georgiev, B. Goodman, *J. Optoelectron. Adv. Mater.* **3**, 703 (2001).
- [11] M. F. Thorpe, D. J. Jacobs, M. V. Chubynski, J. C. Phillips, *J. Non-Cryst. Solids* **266-269**, 859 (2000).
- [12] A. J. Rader, B. M. Hespeneide, L. A. Kuhn, M. F. Thorpe, *Proc. Natl. Acad. of Science* **99**, 3540 (2002).
- [13] J. C. Phillips, *Phys. Rev. Lett.* **88**, 216401 (2002).
- [14] For definitions of T_g used in DSC, see C. A. Angell, ref. 6, p.7. Also see Perkin Elmer Corp., <http://instruments.perkinelmer.com/>.
- [15] C. T. Moynihan, *J. Non - Cryst. Solids* **172-174**, 1395 (1994). *Ibid* **203**, 359 (1996).
- [16] A. Q. Tool, *J. Am. Ceram. Soc.* **29**, 240 (1946), O. S. Narayanaswamy, *J. Am. Ceram. Soc.* **54**, 491 (1971), C. T. Moynihan et al., (N.Y.) *Acad. Sci.* **279**, 15 (1976).
- [17] Liuchun Cai, P. Boolchand, *Phil. Mag. B.* (in press).
- [18] M. Reading, A. Luget, R. Wilson, *Thermochim. Acta* **238**, 295 (1994). Also see *Modulated DSC Compendium*(1997). Reprint # TA Instruments Inc., New Castle, DE, <http://www.tainst.com/>.
- [19] E. Verdonck, K. Schaap, L. C. Thomas, *Intl. J. of Pharmaceutics* **192**, 3 (1999).
- [20] D. G. Georgiev, P. Boolchand, M. Micoulaut, *Phys. Rev. B* **62**, R9228 (2000).
- [21] T. Wagner, S. O. Kasap, *Phil. Mag. B* **74**, 667 (1996).
- [22] L. Carpentier, O. Bustin, M. Descamps, *J. Phys. D: Appl. Phys.* **35**, 402 (2002).
- [23] O. Bustin, M. Descamps, *J. Chem. Phys.* **120**, 10982 (1999).
- [24] N. O. Birge, S. Nagel, *Phys. Rev. Lett.* **54**, 2674 (1985).
- [25] K. L. Ngai, *J. Chem. Phys.* **109**, 6982 (1998).
- [26] J. C. Phillips, *Rep. Prog. Phys.* **59**, 1133 (1996).
- [27] D. Tonchev, S. O. Kasap, *Mat. Sci. Engg A* **328**, 62 (2002).
- [28] P. Boolchand, W. J. Bresser, *Phil. Mag. B* **80**, 1757 (2000).
- [29] P. Boolchand, W. J. Bresser, D. G. Georgiev, Y. Wang, *J. Wells in Phase Transitions and Self-Organization in Electronic and Molecular Networks*, Ed. J. C. Phillips and M. F. Thorpe, Kluwer Academic/ Plenum Publishers, 2001, p. 65.
- [30] M. B. Meyers, E. J. Felty, *MRS Bull.* **2**, 535 (1967).
- [31] R. Kerner, M. Micoulaut, *J. Non-Cryst. Solids* **210**, 298 (1997).
- [32] M. Micoulaut, *Eur. Phys. J. B1*, 277 (1998).
- [33] P. Boolchand, D. G. Georgiev, Tao Qu, Fei Wang, Liuchun Cai, S. Chakravarty, *C. R. Acad. Sci. II C* (in press).
- [34] M. Micoulaut, *C. R. Acad. Sci. II C* (in press).
- [35] L. Tichy, H. Ticha, *J. Non-Cryst. Solids* **189**, 141 (1995).
- [36] B. Effey, R. Cappelletti, *Phys. Rev B* **59**, 4119 (1999).
- [37] Y. Wang, P. Boolchand, M. Micoulaut, *Europhys. Lett.* **52**, 633 (2000).
- [38] S. Mahadevan, A. Giridhar, *J. Non-Cryst. Solids*, **143**, 52 (1995).
- [39] A. Giridhar, S. Mahadevan, *J. Non-Cryst. Solids*, **151**, 245 (1992).
- [40] G. Lucovsky, L. S. Sremaniak, J. L. Whitten, in *Physics and Applications of Disordered Materials*, Ed. M. Popescu, INOE Publ. House, Bucharest, 2002, p. 65.
- [41] M. Zhang, P. Boolchand, *Science* **266**, 1355 (1994).
- [42] R. Kerner, J. C. Phillips, *Solid State Comm.* **117**, 47 (2001).
- [43] J. C. Phillips (private comm.).
- [44] D. Selvanathan, W. J. Bresser, P. Boolchand, B. Goodman, *Solid. St. Comm.* **111**, 619 (1999).
- [45] D. Selvanathan, W. J. Bresser, P. Boolchand, *Phys. Rev. B* **61**, 15061 (2000).
- [46] M. Micoulaut, *Europhys. Lett.* **58**, 830 (2002).
- [47] P. Boolchand, M. F. Thorpe, *Phys. Rev. B* **50**, 10366 (1994).
- [48] P. Boolchand, M. Zhang, B. Goodman, *Phys. Rev. B* **53**, 11488 (1996).
- [49] Y. Wang, J. Wells, D. G. Georgiev, P. Boolchand, K. Jackson, M. Micoulaut, *Phys. Rev. Lett.* **87**, 185503 (2001).
- [50] M. F. Thorpe, D. J. Jacobs, N. V. Chubynsky, A. J. Rader in *Rigidity Theory and Applications*, Ed. M. F. Thorpe and P.M. Duxbury, Kluwer Academic/Plenum Publishers, 1999, p. 239.

- [51] J. Ph. Bouchaud, L. Cugliandolo, J. Kurchan, M. Mézard, *Physica A* **226**, 243 (1996).
- [52] V. Dupuis, E. Vincent, J. Ph. Bouchaud, J. Hamman, A. Ito, H. Aruga Katori, *Phys. Rev. B* **64** 174204 (2001).
- [53] J. M. Saiter, J. Grenet, C. Vautier, *Phil. Mag. B* **64**, 33 (1991).
- [54] I. Prigogine, R. Defay, *Chemical Thermodynamics*, Longman Greens (1954).
- [55] K. Samver, R. Busch, W. L. Johnson, *Phys. Rev. Lett.* **82**, 580 (1999).
- [56] Z. U. Borisova, *Glassy Semiconductors*, Plenum Press, New York (1981).
- [57] P. Viot, G. Tarjus, D. Kivelson, *J. Chem. Phys.* **112**, 10368 (2000).