

# Simple clues and rules for self-organized rigidity in glasses

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A new elastic phase has been recently discovered in glasses of selected compositions. This new phase is found in the vicinity of the network mean coordination number  $\bar{r} = 2.4$  that marks the onset of rigidity in a glassy network with increasing connectivity. Here, it is shown that in contrast with random networks where rigidity percolates at the single threshold of  $\bar{r} = 2.4$ , networks that are able to self-organize to avoid stressed rigid local bonding will remain in an almost stress-free state during a compositional interval, an intermediate phase (or Boolchand phase), that is bounded by a flexible phase and a stressed rigid phase. The details of the theoretical construction are given for Ge-Se or Ge-Te systems.

(Received October 8, 2007; accepted October 9, 2007)

*Keywords:* Self-organization, Rigidity, Glasses, Ge-Se, Ge-Te

## 1. Introduction

Concepts from global rigidity in networks found their origin from Lagrangian constraint counting in mechanics [1] and have been applied with great success in glass science for several decades [2]. Bonds in a glass network can indeed be considered as constraints arising from interatomic stretching and bending forces. The connectivity or cross-link density (best quantified by the network mean coordination number  $\bar{r}$ ) plays therefore a key role. In highly cross-linked networks where  $\bar{r}$  is large, there are more constraints than degrees of freedom per atom on average and the structure is stressed rigid (hyperstatic or overconstrained). At low connectivity, one has a flexible (hypostatic or underconstrained) structure that contains more degrees of freedom than constraints. Thorpe [3] analyzed the vibrational behaviour of such kind of networks and identified a mean-field (MF) floppy to rigid transition when the mean coordination number equals  $\bar{r} = \bar{r}_c = 2.38$ , a result that agrees with global (Maxwell) constraint counting as enunciated by Phillips [4] from the enumeration  $n_c$  of the number of constraints corresponding to bond stretching and bond bending forces.

The underlying nature of this peculiar transition has been strongly reconsidered recently because two transitions at  $\bar{r}_{c(1)}$  and  $\bar{r}_{c(2)}$  have been found [5] experimentally in a variety of glasses. These define an intervening region (or intermediate phase, (IP)) between the floppy and the stressed rigid phase. The most obvious characterisation of the IP has come from complex heat flow measurement at the glass transition of chalcogenides that show a vanishing (or at least a minimum) of a non-reversing heat flow. The latter captures most of the kinetic events arising from the slowing down of the dynamics, and the vanishing of this

quantity suggests that glasses (out of equilibrium) and liquids (in equilibrium) are very similar in the Intermediate Phase. Glasses in the IP display furthermore some remarkable properties such as absence of ageing [6] or stress [7], selection of isostatically rigid local structures [5] or weak birefringence [8]. The two boundaries have been characterized from numerical calculations [9] and cluster analysis [10] on self-organized networks and identified as being a rigidity transition at low  $\bar{r}$  and a stress transition at high  $\bar{r}$ . In the mean-field (or global) approach, or in random networks where self-organization does not take place, both transitions coalesce into a single one. Moreover, links between IP and protein folding [11], high-temperature superconductors [12] or computational phase transitions [13] have been stressed that go much beyond simple analogies.

The understanding of the IP is therefore of general interest. It has become clear that stress avoidance in the network is responsible for the width  $\Delta\bar{r} = \bar{r}_{c(2)} - \bar{r}_{c(1)}$  and the location of the intermediate phase, an idea that has gained some strength from energetical adaptation in a simple random bond model [14] for the rigidity transition or suppressed nucleation of rigidity during a fluid-solid transition [15]. Mousseau and co-workers [16] have also shown recently that critical self-organization with equilibration on diluted triangular lattices would lead to an intermediate phase.

In glasses, current promising applications of these ideas on self-organized rigidity have been found in solid electrolytes where the degree of flexibility controls the ionic conduction [17], or in phase changing materials [18]. And since it has been found that these concepts are not restricted to chalcogenides (i.e. network-forming glasses of the form e.g.  $A_xSe_{1-x}$ ) as previously believed [19], it suggests that all glasses can be classified in terms of flexible, intermediate, stressed rigid from their mechanical

or thermal properties, provided that the average coordination number lies in the range where self-organization can take place.

This paper shows how topological size increasing cluster constructions allow for a description that goes beyond global rigidity and the single threshold at  $\bar{r} = 2.4$ . These constructions highlight the effect of the deviation from network randomness that is achieved by selective cluster growth rules leading to structural self-organization and leads to an intermediate phase. A simple application for  $Ge_xSe_{1-x}$  and  $Ge_xTe_{1-x}$  glasses is presented and analyzed.

## 2. Global rigidity in amorphous networks

Global rigidity derived from the Maxwell-Lagrange approach is based on the enumeration of nearest-neighbour forces between atoms that can be modelled for small displacements from the equilibrium structure by a harmonic Kirkwood – Keating potential [20] that contains bond-stretching and bond-bending interactions. Interactions are thus translated into bonding constraints in this approach that neglects more weaker forces (see however [21]).

The total number of internal degrees of freedom (or floppy modes) can be computed by counting the number of bond-stretching and bending forces of a  $r$ -coordinated atom, which gives respectively  $r/2$  and  $(2r-3)$  constraints when all constraints are considered as intact. Note that if some bond-bending constraints are broken [as for O in  $SiO_2$  [22] or Ba in barium silicates [23] ], the corresponding count is modified appropriately. The total number of constraints is then:

$$n_c = \frac{\sum_{r \geq 2} n_r [r/2 + (2r - 3)]}{\sum_{r \geq 2} n_r} \quad (1)$$

with  $n_r$  being the concentration of atoms with coordination  $r$  and  $N = \sum_{r \geq 2} n_r$  is the total number of atoms of the

network. In a three-dimensional network, the fraction  $f$  of floppy modes is then given by:  $f = 3 - n_c$  that can be simply rewritten as a function of the network mean coordination

number  $\bar{r} = \frac{1}{N} \sum_{r \geq 2} r n_r$ :

$$f = 2 - \frac{5}{6} \bar{r} \quad (2)$$

It is easy to check that  $f$  vanishes when the mean coordination number  $\bar{r}$  reaches the magic value of  $\bar{r}_c = 2.4$ . Depending on which system is under investigation, one can attain this value by various compositions, especially in ternary glasses.

From Thorpe's work on random networks [3], it is known that the location at  $\bar{r}_c = 2.4$  defines a *single*

transition between a flexible and a rigid phase. The boundary defines a rigidity transition bringing an underconstrained network to an overconstrained one. Typical experimental manifestations of this transition can be found in III-VI (e.g.  $Ga_xS_{1-x}$ ,  $x_c = 0.40$ ), IV-VI ( $Ge_xSe_{1-x}$ ,  $x_c = 0.20$ ) or V-VI ( $As_xSe_{1-x}$ ,  $x_c = 0.40$ ) network glasses but also in binary electrolytes such as silicates [19] or tellurates [22].

The existence of a single transition obviously runs against the now generally accepted observation of the heat flow minimum defining the Boolchand intermediate phase [5] and the two vibrational thresholds that are detected from Raman experiment. The theoretical question one has therefore to deal with is “*How can two thresholds be obtained from a construction that contains ingredients of the initial (global) construction based on bonding constraints?*” A basic observation is that the single transition at mean coordination number 2.4 is obtained when constraint counting is performed at a global level without any consideration of the presence of correlated fluctuations of e.g. stress-free rigidity that may permit to delay the onset of stressed rigidity when  $\bar{r}$  is steadily increased. One has furthermore to remember that the corresponding eigenmode analysis [3] is realized on networks with bonds being removed at random. What will happen if bonds are removed in a selective fashion? Finally, one has to note that the theoretical framework described above only relies on the coordination number of the local structures which are directly defined by the macroscopic concentration. Both approaches (constraint counting or floppy mode analysis) therefore define a mean-field result where neither typical length-scales nor any spatial correlations of the emerging elastic phases (stress free, stressed) are involved.

In the following, a new theoretical method is described. This method allows to start from the local structure as in the global approach. The difference with the latter lies in the fact that one is now able to create structural correlations yielding a self-organized network and a Boolchand Intermediate Phase.

## 3. Self-organized networks

### 3.1 Cluster construction

The framework (see [10], [24]) described here uses size increasing cluster approximations (SICA) combined with constraint counting that permits to generate the Boolchand Intermediate Phase, starting from the local structural level (e.g. the  $Se$  atom and the  $GeSe_{4/2}$  tetrahedron in  $Ge-Se$  binary). Therefore, the initial step of the method will always lead to the single Phillips-Thorpe transition. In fact, as already mentioned above, constraint counting in global rigidity is performed either on local structures (e.g.  $AsSe_{3/2}$  species and  $Se$  chain fragments) or on the macroscopic concentration ( $n_c = 2 + x$  in  $As_xSe_{1-x}$ ) which leads in both cases to a single rigidity transition satisfying  $f = 0$  (e.g.  $x = 0.40$  in  $As_xSe_{1-x}$ ).

The SICA construction starts from the usual mean-field treatment of rigidity, where the probabilities of the local structures are derived from the macroscopic modifier concentration (e.g.  $x$  in  $Ge_xSe_{1-x}$ ). This corresponds to a basic level ( $l=1$ ) out of which size increasing clusters ( $l=2, l=3, \dots$ ) are generated and their probabilities  $p_i^{(l)}$  ( $i=1 \dots N_l$ ) computed. The latter depend on the basic probabilities at  $l=1$ , statistical (cluster degeneracy) and Boltzmann factors (see example in Table I or in [10],[19], [24]).  $N_l$  represents here the total number of created clusters at a given step  $l$ .

### 3.2 Constraint counting procedure

Once the clusters are generated and their probabilities evaluated, one applies constraint counting algorithms on these clusters by enumerating each bond-stretching and bond-bending forces, following the counting introduced by

Thorpe [3]. Special care is taken for closed structures such as rings, which can contain for low enough sizes some extra constraints that need to be removed. At step  $l$ , the number of floppy modes of the network is then given by:

$$f^{(l)} = 3 - n_c^{(l)} = 3 - \frac{\sum_{i=1}^{N_l} n_{c(i)} p_i^{(l)}}{\sum_{i=1}^{N_l} N_i p_i^{(l)}} \quad (3)$$

where  $n_{c(i)}$  and  $N_i$  are respectively the number of mechanical constraints and the number of atoms of the cluster with probability  $p_i^{(l)}$ . An example of such counting is provided in Table I. It shows that the clusters lead to bonding types with a well-defined mechanical character: flexible ( $n_c < 3$ ), isostatically rigid (stress-free,  $n_c = 3$ ) and stressed rigid ( $n_c > 3$ ).

Table 1. Possible local structures and possible generated clusters at step  $l=1$  and  $l=2$  in the SICA construction, together with the cluster connectivity  $R_i$ . In square brackets are given the number of different isomers for a given cluster stoichiometry.

System	Basic local Structure $l=1$	Possible clusters $l=2$	$R_i$ $l=2$	Possible clusters $l=3$	$R_i$ $l=3$
$Ge_xSe_{1-x}$	$GeSe_{4/2}$ $Se_2$	$Se_4$ $GeSe_4$ $CS-Ge_2Se_4$ $ES-Ge_2Se_4$	2 4 6 4	$Se_6$ $GeSe_6$ $Ge_2Se_6$ [3] $Ge_3Se_6$ [3]	2 4 4 6 6 4 6 8
$Ge_xTe_{1-x}$	$GeTe_{6/2}$ $Te_2$	$Te_4$ $GeTe_5$ $CS-Ge_2Te_6$ $ES-Ge_2Te_6$	2 6 10 6	$Te_6$ $GeTe_7$ $Ge_2Te_8$ [3] $Ge_3Te_9$ [3]	2 6 8 10 10 10 12 14
$(1-x)SiS_2$ $xNa_2S$	$Q^4$ $Q^3$	$Q^4-Q^4$ $Q^4-Q^3$ $Q^3-Q^3$	6 5 4	$Q^4-Q^4-Q^4$ [3] $Q^4-Q^4-Q^3$ [6] $Q^4-Q^3-Q^3$ [6] $Q^3-Q^3-Q^3$ [3]	

Self-organization is achieved as follows. Starting from all possible flexible clusters in which stressed rigid non-cyclic (dendritic) connections are absent (i.e. no corner-sharing  $GeSe_{4/2}$  tetrahedra having  $n_c > 3$ ), and increasing the connectivity (via  $\bar{r}$ ), one constructs all possible clusters by avoiding a dendritic (non cyclic) stressed rigid connection. This amounts to have selection rules in the cluster construction with growing step  $l$ . Then, one can investigate at which composition the network will have a vanishing of the number of floppy modes  $f^{(l)}$ , following the usual definition of the rigidity transition. However, because of the absence of the stressed rigid dendritic connections, stress can not propagate with increasing  $\bar{r}$ . On the other hand, stressed rigidity in small rings is allowed. Once the rigidity transition is bypassed, these selective rules can hold for a while but only up to a certain point in connectivity where the network will not be able to avoid stressed rigid dendritic clusters any more. This defines a stress transition in rigidity theory and can not be

found from a mean-field (global) treatment. Simple examples of such a construction are provided below.

## 4. Results

### 4.1 Germanium and silicon selenide and sulphide networks

Using the described construction, one is able to compute at different levels of approximations the behaviour of Group IV chalcogenide network formers such as  $Ge_xS_{1-x}$  or  $Si_xSe_{1-x}$ , but also  $Ge_xTe_{1-x}$ . We sketch here the detail of the construction for the elementary step  $l=2$  that leads already to an intermediate phase, provided that edge-sharing structures can exist.

At step  $l=1$ , one computes the probability for the generated structures:

$$p(Se_4) = \frac{4(1-p)^2 e_{flex}}{4(1-p)^2 e_{flex} + 16p(1-p)e_{iso} + 16p^2 e_{stress} + 72p^2 e_{ring}} \quad (4)$$

$$p(GeSe_4) = \frac{16p(1-p)e_{iso}}{4(1-p)^2 e_{flex} + 16p(1-p)e_{iso} + 16p^2 e_{stress} + 72p^2 e_{ring}} \quad (5)$$

$$p(CS - Ge_2Se_4) = \frac{16p^2 e_{stress}}{4(1-p)^2 e_{flex} + 16p(1-p)e_{iso} + 16p^2 e_{stress} + 72p^2 e_{ring}} \quad (6)$$

$$p(ES - Ge_2Se_4) = \frac{72p^2 e_{ring}}{4(1-p)^2 e_{flex} + 16p(1-p)e_{iso} + 16p^2 e_{stress} + 72p^2 e_{ring}} \quad (7)$$

with  $p=2x/(1-3x)$  and  $x$  the concentration of Group IV atoms. The clusters  $CS-Ge_2Se_4$  and  $ES-Ge_2Se_4$  correspond respectively to two corner-sharing and edge-sharing  $GeSe_{4/2}$  tetrahedra. One should also note that the Boltzmann factors  $e_i$  (with  $i=flex, iso, stress, ring$ ) involve a corresponding energy gain  $E_i$ , depending on the mechanical nature of the generated cluster (flexible, isostatically rigid, stressed rigid, ring or cyclic stressed rigid). Out of the cluster probabilities, the Group IV concentration can be evaluated:

$$p = \frac{2x}{1-x} = \frac{8p(1-p)e_{iso} + 16p^2 e_{stress} + 72p^2 e_{ring}}{4(1-p)^2 e_{flex} + 16p(1-p)e_{iso} + 16p^2 e_{stress} + 72p^2 e_{ring}} \quad (8)$$

and leads by solving (8) to the evaluation of  $e_{flex}/e_{iso}$  or the energy difference  $E_{iso}-E_{flex}$ :

$$\frac{e_{flex}}{e_{iso}} = 2 \frac{1-5x + 4x \frac{e_{stress}}{e_{iso}} + 18x \frac{e_{ring}}{e_{iso}}}{1-3x} \quad (9)$$

which is a positive function of the concentration  $x$ . The vanishing of  $e_{flex}/e_{iso}$  in equ. (7) takes place when flexible connections have entirely disappeared and the corresponding concentration  $x=x_{c(2)}$  corresponds to the stress transition. Noteworthy is that in absence of stressed rigid ( $e_{stress}=0$ ) and ring structures ( $e_{ring}=0$ ), one recovers the location of the global constraint counting approach at  $x_c=0.20$ . The stress transition composition  $x_{c(2)}$  can be also found by solving the concentration equation (8) in terms of  $e_{stress}/e_{iso}$  (instead of  $e_{flex}/e_{iso}$ ) so that the this peculiar composition is given by :

$$x_{c(2)} = \frac{1}{5-18 \frac{e_{ring}}{e_{iso}}} \quad (10)$$

From the simple example displayed here, one sees that a system with a large fraction of edge-sharing units, will have a stress transition shifted to higher compositions. An additional delay would be achieved by allowing in the flexible and intermediate phase some fraction of stressed rigid corner-sharing connections (represented by  $CS-Ge_2Se_4$  clusters which would correspond to a non-zero value for  $e_{stress}/e_{iso}$  in equ. (9)).

Equation (3) finally allows to compute the number of floppy modes of the system given the probability of the clusters and the Boltzmann factors and leads for  $x < x_{c(2)}$  to:

$$f^{(l)} = (1-5x) \frac{1-3x + 18x \frac{e_{ring}}{e_{iso}}}{(1+5x)(1-3x) + 18x \frac{e_{ring}}{e_{iso}} (1+3x)} \quad (11)$$

Here one sees that the number of flexible modes  $f^{(l)}$  will always vanish at  $x=x_{c(1)}=0.20$  which designates the rigidity transition.

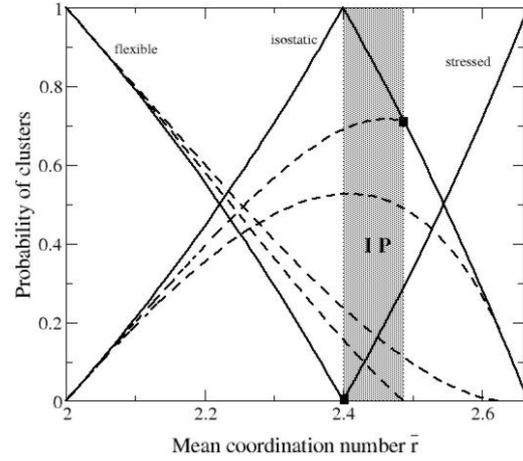


Fig. 1. Probability of finding flexible, intermediate (stress-free) and stressed rigid clusters in a tetrahedral (Ge-Se) IV-VI network for a zero (solid line) or different fractions of edge-sharing tetrahedral (broken lines). The dashed area defines the intermediate phase.

In summary, one sees that SICA allows for a description that goes beyond the mean-field approach. The cluster construction is realized by building larger structures in a systematic scheme and the latter relies on the local structures that can be related to the cross-link concentration  $x$ . In terms of rigidity transitions, it becomes clear that the stiffening of the network is achieved by the presence of weakly stressed rigid units represented at the lowest approximation by edge-sharing  $GeSe_{4/2}$  tetrahedra. But at a fixed rate of edge-sharing tetrahedra and still increasing the cross-link density, one will finally reach a point beyond which dendritic stress can not be avoided anymore. This composition represents the stress transition and in fact. For larger compositions, the mean cluster connectivity  $R^{(l)}$  defined by:

$$R^{(l)} = \frac{1}{l+1} \sum_i R_i p_i^{(l)} \quad (12)$$

will suddenly increase (Fig. 2) since the number of possible connections provided by the onset of corner-sharing  $GeSe_{4/2}$  connections is 6. Here  $R_i$  designates the coordination number of a cluster (see Table I).

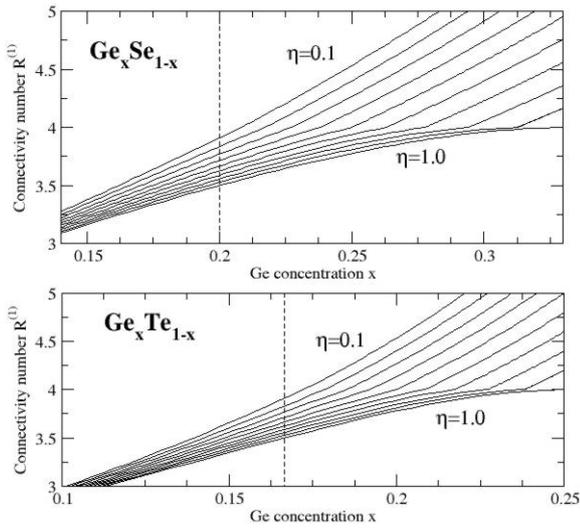


Fig. 2. Mean cluster connectivity  $R^{(2)}$  at step  $l=2$  in a tetrahedral and an octahedral IV-VI glass system for different fractions of edge-sharing polyhedra ranging from 0.1 to 1.0 by steps of 0.1.

In the intermediate phase when  $x_{c(1)} < x < x_{c(2)}$ , the network structure is then made of flexible chain parts, isostatically rigid  $GeSe_4$  connections and edge-sharing tetrahedral. The clue of the opening of the intermediate phase is the self-organized nature of the network. Indeed, if the probabilities were only given by their statistical weight (in other words, setting in the construction all  $e_i=1$ ) would lead to a single transition satisfying  $x=0.20$ . Note finally that for larger cluster sizes, various kinds of rings can contribute as well.

#### 4.2 Group IV tellurides

The germanium and silicon tellurides should display a slightly different behaviour in terms of non-mean field rigidity because the local structure is found to be of octahedral type. In fact, both neutron diffraction [25] and first principles [26] studies show that there are six tellurium neighbours in the vicinity of a germanium. The origin of this peculiar local environment arises from the fact that there is no stable crystalline compound [27] at  $x=0.33$  germanium but instead a  $GeTe$  (at  $x=0.50$ ) and  $Si_2Te_3$  (at  $x=0.40$ ) leading to the absence of a tetrahedral network such as  $Ge-Se$ .

However, a closer examination of the nature of the local bonding types from e.g. the partial  $Ge-Te$  pair distribution function shows that the fifth and the sixth tellurium neighbours have a much larger spatial extension [28]. It suggests that their bond-stretching forces are intrinsically broken and the same holds for the bond-bending forces. From a simple bond constraint counting, this leads therefore to the same global rigidity threshold as for the selenides, and manifests experimentally in e.g. space-filling tendency around  $x=0.18$ .

In terms of cluster probabilities, since the local structure is different one should have different statistical factors appearing in the SICA construction. Let us define the  $Te_2$  and the  $GeTe_{6/2}$  as basic local structures. For the first level of approximation, one will have the probability of a  $GeTe_5$  cluster given by:

$$p(GeTe_5) = \frac{24p(1-p)e_{iso}}{4(1-p)^2e_{flex} + 24p(1-p)e_{iso} + 36p^2e_{stress} + \frac{225}{2}p^2e_{ring}} \quad (11)$$

with  $p=2x/(1-2x)$ . Once the whole structural and rigidity analysis performed, one is able to obtain an intermediate phase defined by the boundaries:

$$x_{c(2)} = \frac{1}{2(3 - \frac{e_{ring}}{e_{iso}})} \quad (12)$$

and  $x_{c(1)}=1/6=0.167$  corresponding respectively to the stress and rigidity transition.

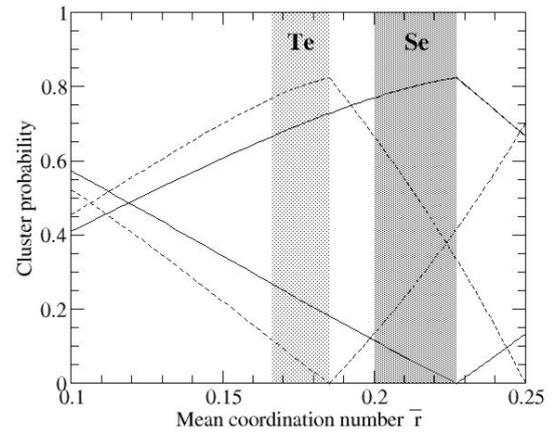


Fig. 3. Probability of finding flexible, intermediate (stress-free) and stressed rigid clusters in a tetrahedral ( $Ge-Se$ , solid lines) and octahedral ( $Ge-Te$ , broken lines) IV-VI network for a fraction of 0.3 edge-sharing polyhedra. The dashed areas define the respective  $Ge-Se$  and  $Ge-Te$  intermediate phases.

The behaviour of a telluride model is depicted in Fig. 3. It shows that for an equivalent rate of edge-sharing polyhedra, rigidity onsets earlier in a  $Te$  base glass compared to the  $Se$  based glass. This is not surprising since the connectivity of a tellurium glass is higher due to the octahedral local structure. This also implies that the statistical weights of the SICA cluster probabilities involving the  $GeTe_{6/2}$  unit will be higher. But the thresholds still manifest at compositions close to  $x=0.20$  because of the partial broken  $Ge-Te$  bonding constraints.

Experimentally, this is seen from molar volume minima in  $Ge-Te$  and  $Ge-Se$  systems that are respectively found at the compositions of  $x=0.18$  [29] and  $x=0.20$  [30].

In summary, we have shown that from a cluster construction based on the local structure of a glass, one

was able to recover under various possibilities the salient features on global and self-organized rigidity. It appears that a Boolchand Intermediate Phase is mainly obtained when stressed rigidity nucleates in small ring structures, a situation that can hold with increasing cross-link density only up to a certain point beyond which the proliferation of highly connected (large  $R_i$ ) stressed rigid units allow for percolation of stressed rigidity.

### Acknowledgements

It is a pleasure to acknowledge ongoing discussions with P. Boolchand, M. Malki, N. Mousseau, and P. Simon. LPTMC is Unité Mixte de Recherche du Centre National de la Recherche Scientifique (CNRS) n. 7600.

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