Europhys. Lett., **58** (6), pp. 830–836 (2002)

Rigidity transitions and constraint counting in amorphous networks: Beyond the mean-field approach

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(received 7 February 2002; accepted in final form 27 March 2002)

PACS. 61.43.Fs – Glasses. PACS. 62.20.-x – Mechanical properties of solids.

Abstract. – We study rigidity transitions in covalent amorphous networks using size-increasing cluster approximations and constraint-counting algorithms. Possible consequences of the presence of self-organization are examined. The analysis reveals two transitions instead of the usual (mean-field) single transition: one from a floppy to an isostatic rigid phase at a mean coordination number \bar{r}_{c1} where the number of floppy modes vanishes and a second one from an isostatic to a stressed rigid phase at \bar{r}_{c2} . The value of the two critical mean coordination numbers as well as the width $\Delta \bar{r} = \bar{r}_{c2} - \bar{r}_{c1}$ of the intermediate phase depend very strongly on the presence of medium-range order elements such as rings.

Introduction. – The notion of constraints and their application to classical macroscopic physics problems such as the stability of bridges and trusses have been introduced and first considered by Lagrange and Maxwell [1,2]. On this basis, Phillips asserted [3,4] some twenty years ago that covalent networks can be mechanically constrained by interatomic valence forces such as bond-stretching and bond-bending and optimal glass formation is attained when the network sits at a mechanically critical point. This happens when the constraints n_c per atom estimated by Maxwell counting equal the degrees of freedom per atom in 3D, *i.e.* $n_c = 3$.

Such mechanical systems have been examined in terms of percolation theory by Thorpe [5] who showed by a normal mode analysis that the number of zero frequency solutions (floppy modes) f of the dynamical matrix equals $f = 3 - n_c$ and vanishes when the mean coordination number \bar{r} of the network reaches the critical value $\bar{r}_c = 2.4$. In this mean-field approach, one considers a network of N atoms composed of n_r atoms that are r-fold coordinated. The enumeration of mechanical constraints in this system gives r/2 bond-stretching constraints and (2r-3) bond-bending constraints for an r-fold coordinated atom. Since then, a certain number of structural possibilities have been taken into account such as rings, broken bond-bending constraints [6] or the effects of one-fold coordinated atoms [7]. These powerful ideas have led to the prediction of a floppy-to-rigid transition in random networks and various examples where rigidity percolation threshold occurs have been reported [8]. Also, applications of rigidity in biology and computational science have been reported [9, 10]. Nevertheless, experiments on binary and ternary chalcogenide glasses have shown the existence of two transitions at \bar{r}_{c1} and \bar{r}_{c2} instead of the single mean-field transition [11–13], suggesting that the mean-field constraint counting alone, as has been realized up to now, may be insufficient to accurately describe the

underlying phase transitions. These transitions show up in Raman scattering experiments where characteristic mode frequencies display a marked change in behavior. For $\bar{r} < \bar{r}_{c1}$ these frequencies are almost composition independent whereas for $\bar{r} > \bar{r}_{c2}$ they show a power law behavior [13], consistently with numerical calculations [14]. In the intermediate region, a linear increase is observed [13]. Also, modulated differential scanning calorimetry (MDSC) realized on different chalcogenide glasses shows that in the intermediate region $\bar{r}_{c1} < \bar{r} < \bar{r}_{c2}$, the non-reversing heat flow almost vanishes, suggesting evidence [15] for the growth of a selforganized (isostatic rigid) intermediate phase between the floppy and the stressed rigid phases, for which evidence is also obtained from numerical simulations [16].

However, a certain number of questions remain at this stage. What controls the values \bar{r}_{c1} and \bar{r}_{c2} , the width $\Delta \bar{r} = \bar{r}_{c2} - \bar{r}_{c1}$? Recent results show that this width can be particularly sharp [17]. How does isostatic regions and self-organization influence the absolute magnitude of these quantities? What can be done which goes beyond the elegant mean-field approach? This letter attempts to address these basic issues. We report here on the role of medium-range order (MRO) in glasses of the form $B_x A_{1-x}$ with coordination numbers $r_A = 2$ and $r_B = 4$, and $\bar{r} = 2 + 2x$. Typical glasses are the Group-IV chalcogenides such as $\text{Ge}_x \text{Se}_{1-x}$ or $\text{Si}_x \text{Se}_{1-x}$ which have been extensively studied in this context. To construct MRO, we have used size-increasing cluster approximations (SICA) to generate sets of clusters on which we have applied constraint-counting algorithms. The results show two transitions, one at which the number of floppy modes vanishes. Another transition (a "stress transition") where stress in the structure cannot be avoided anymore, is located beyond. In between, this provides evidence for a self-organized network for which the probability of stress-free clusters has been computed. The width $\Delta \bar{r}$ increases with the fraction of MRO elements. Finally, in case of random bonding, a single transition is obtained.

Construction. – SICA have been first introduced to elucidate the formation of borate glasses [18] and fullerenes [19], but also to infer the intermediate-range order in amorphous semiconductors [20]. They rely on the statement that the fraction of significant MRO structures converges very rapidly to a limit value when the size of the considered clusters is increasing [21]. The construction is realized in Grand Canonical Ensemble with particular energy levels. One starts from short-range order molecules (the basic units at the initial step l=1which will serve as building blocks) and construct all possible structural arrangements of two basic units (l = 2), see table I), three basic units (l = 3) and so on. This is supposed to be realized at the formation of the network, when T equals the fictive temperature $T_{\rm f}$ which is defined by the intersection of the extrapolated supercooled liquid and glass curves [22]. Here, we have chosen as basic units the A_2 and the stoichiometric balanced BA_2 molecules (e.g., Se_2 and $GeSe_2$) for a reason which will become clear below. We have checked that the results do not depend on this particular initial choice. These basic units coming from an infinite reservoir have respective probabilities 1-p and p=2x/(1-x), x being the concentration of B atoms. The creation of a chain-like A_2 - A_2 structure will involve a chemical potential gain of E_1 , isostatic A₂-BA₂ bondings will use a chemical potential gain of E_2 and the creation of corner-sharing (CS) and edge-sharing (ES) $BA_{4/2}$ tetrahedra, respectively, E_3 and E_4 . The latter quantity will be used to tune the fraction of ES among the structure. The produced probabilities have different statistical weights which correspond to the number of equivalent ways a given cluster can be constructed. This quantity can be regarded as the degeneracy of the corresponding energy level (see fig. 1). For instance, given the coordination number 4 of the basic unit $BA_{4/2}$ and labeled covalent bonds a CS B_2A_4 cluster has the multiplicity 4×4 ,

whereas for a ES cluster, we count $2 \times \begin{pmatrix} 4 \\ 2 \end{pmatrix} \begin{pmatrix} 4 \\ 2 \end{pmatrix} = 72$ in three dimensions.



Fig. 1 – Some of the MRO clusters generated by SICA at step l = 3 with their statistical weight. a) A six-membered ring with $n_c = 3.67$. b) An edge-sharing tetrahedra chain typical of vitreous SiSe₂ with $n_c = 3.22$. c) A six-membered ring with chalcogen inclusions and $n_c = 3.25$.

Due to the initial choice of the basic units, the value of the chemical potential E_2 will influence the probability of isostatic clusters since this quantity is involved in the probability of the isostatic BA₄ cluster ($n_c = 3$, see table I). If we have $E_2 \ll E_1, E_3, E_4$, the network will be mainly isostatic.

At step l = 2, we can generate three types of clusters (table I), A₄, BA₄ and B₂A₄ having two isomers (the CS and ES tetrahedra). Their unrenormalized probabilities are given by $p_{A_4} = 4(1-p)^2 e_1$, $p_{BA_4} = 16p(1-p)e_2$, $p_{CS} = 16p^2 e_3$ and $p_{ES} = 72p^2 e_4$ out of which the concentration $x^{(l=2)}$ of B atoms can be extracted. The quantities $e_i = \exp[-E_i/T_f]$ are the Gibbs weights at T_f . Next, we compute the number of mechanical constraints (bond-bending and bond-stretching) per atom on each cluster by Maxwell counting. Special care has to be taken in order to avoid the counting of redundant constraints on clusters containing rings, following the procedure described by Thorpe [5]. The probabilites depend on two parameters (*i.e.* the Gibbs weights e_1/e_2 and e_3/e_2) and eventually e_4/e_2 if one considers the possibility of ES or rings. One of these two weights can be calculated by writing a conservation law for the concentration of B atoms [23]:

$$x^{(l)} = x \,. \tag{1}$$

These weights become composition dependent in solving eq. (1) which means that either the chemical potentials E_i or the fictive temperature $T_{\rm f}$ depend on x [22] but here only the $e_i(x)$ -dependence is relevant for our purpose. With increasing cluster size, it is obvious that the number of potential isomers will increase (table I), and also the different types of rings which have some evidence in chalcogenides [24]. We have realized the construction up to the step l = 4. At each step, we have determined either e_1/e_2 or e_3/e_2 solving eq. (1) and computed the total number of constraints n_c per atom on the set of clusters (see table I). Finally, we have looked for the concentration of B atoms (or the mean coordination number \bar{r}) for which the number of floppy modes vanishes.

Results. – Random bonding is obtained by setting the above-defined Gibbs weights e_i to one and the cluster probabilities are then only given by their statistical weights. Solving f = 0, one obtains a single transition for all steps in the mean coordination number range [2.231, 2.275], somewhat lower than the usual mean-field value. This comes from the fact that the number of equivalent ways to connect $BA_{4/2}$ units together is substantially higher than for the connection of (chain-) A_2 units. We do not obtain an intermediate phase in the case of random bonding.

TABLE I – Clusters generated at the different SICA steps l with the chemical formula in case of $\operatorname{Ge}_x \operatorname{Se}_{1-x}$ glasses, the number of isomers and the number of constraints n_c per atom. The number of clusters containing rings is indicated in brackets. GeSe₄ and Ge₂Se₈ are isostatic clusters with respective energy levels E_2 and $2E_2$.

Size <i>l</i>	Cluster	Number of isomers	$n_{ m c}$	
1	Se_2	1	2	
	GeSe_2	1	3.67	
2	Se_4	1	2	
	GeSe_4	1	3	
	$\mathrm{Ge}_2\mathrm{Se}_4$	2(1)	3.67	
3	${ m Se}_6$	1	2	
	GeSe_6	2	2.71	
	Ge_2Se_6	4(2)	3.25	
	$\mathrm{Ge}_3\mathrm{Se}_6$	4(3)	3.67	
4	Se_8	1	2	
	$GeSe_8$	3	2.56	
	$\mathrm{Ge}_2\mathrm{Se}_8$	11(6)	3	
	$\mathrm{Ge}_3\mathrm{Se}_8$	12(9)	3.36	
	$\mathrm{Ge}_4\mathrm{Se}_8$	10(9)	3.67	

Let us turn to self-organization and proceed as follows. Starting from a floppy cluster of size l (almost a chain-like structure made of A atoms), we allow the agglomeration of a new basic unit onto this cluster to generate the cluster of size l + 1 only if the creation of a stressed rigid region can be avoided on this new cluster (due to the agglomeration of a $BA_{4/2}$ basic unit onto another $BA_{4/2}$ tetrahedron being part of the *l*-sized cluster). With this rather simple rule, upon increasing \bar{r} we will accumulate isostatic rigid regions on the size-increasing clusters because $BA_{4/2}$ units are only accepted in A_2 - $BA_{4/2}$ isostatic bondings. Alternatively, we can start from a stressed rigid cluster which exists at higher mean coordination number $(\bar{r} \leq 2.67)$ and follow the same procedure but in opposite way, *i.e.* we allow only bondings which lead to isostatic rigid regions, excluding systematically the possibility of floppy A_2-A_2 bondings. Here, the simplest case deals with dendritic clusters, where we have removed all possibilities of ring creation. For $l \to \infty$, this would permit to recover the results on Random Bond Models [25] for which there are no loops or rings in the thermodynamic limit and to obtain equivalence with Bethe lattice solutions [26]. We obtain a single transition for even l steps at exactly the mean-field value $\bar{r} = 2.4$, whereas for the step l = 3 there is a sharp intermediate phase defined by f = 0 (again at $\bar{r} = 2.4$) and the vanishing of floppy regions (*i.e.* e_1/e_2 is zero) at $\bar{r} = 2.382(6)$. The probability of isostatic clusters as a function of the mean coordination number has been computed and shows that the network is entirely stress free at the point where f = 0 (solid line, fig. 2). If there is a width (for l = 3), then the same probability is less than one and displays a narrow distribution.

Next, we have allowed a certain amount of medium-range order (MRO) by setting the quantity $e_4/e_2 \neq 0$. Two transitions are then obtained for every SICA step. The first one is at \bar{r}_{c1} where the number of floppy modes vanishes. The second one is at \bar{r}_{c2} . When starting from a floppy network close to $\bar{r} = 2$ and allowing only isostatic bondings, there is a point beyond which stressed rigid regions created by the connection of at least two BA_{4/2} units cannot be avoided anymore. This is the definition of the point at \bar{r}_{c2} . Mathematically, this is translated in the SICA approach by a non-zero Gibbs weight e_3/e_2 , and is composition dependent in the region $\bar{r}_{c2} < \bar{r} < 2.67$. We call this point the "stress transition". We show



Fig. 2 – Probability of floppy, isostatic rigid and stressed rigid clusters as a function of the mean coordination number for different fractions of ES at l = 2. The solid lines correspond to the dendritic case where no edge-sharing tetrahedra are allowed. The broken lines correspond to the same quantities for ES fraction at the stress transition of 0.156, 0.290 and 0.818. For an ES fraction of 0.156, the filled squares indicate the point \bar{r}_{c2} at which the stress transition occurs and serves to define the intermediate phase $\Delta \bar{r}$.

the l=2 result (fig. 2) where f=0 at $\bar{r}_{\rm c1}=2.4$ for different fractions of ES tetrahedra, defining an intermediate phase $\Delta \bar{r}$. \bar{r}_{c1} does not depend on the ES fraction, as well as the fraction of stressed rigid clusters in the structure. To ensure continuous deformation of the network when B atoms are added and keeping the sum of the probability of floppy, isostatic rigid and stressed rigid clusters equal to one, the probability of isostatic rigid clusters connects the isostatic solid line at \bar{r}_{c2} . Stressed rigid rings first appear in the region $\bar{r}_{c1} < \bar{r} < \bar{r}_{c2}$ while chain-like stressed clusters (whose probability is proportional to e_3) occur only beyond the stress transition, when $e_3 \neq 0$. We conclude that when \bar{r} is increased, stressed rigidity nucleates through the network starting from rings. Results remain similar for the even l = 4step. It appears from fig. 2 that the width $\Delta \bar{r} = \bar{r}_{c2} - \bar{r}_{c1}$ of the intermediate phase increases with the fraction of MRO. We have represented this quantity as a function of the MRO fraction at the rigidity transition in fig. 3, which shows that $\Delta \bar{r}$ is almost an increasing function of the ES fraction as seen from the result at SICA step l = 4. Here, there is only a small difference between allowing only four-membered rings (ES) (lower dotted line) or rings of all sizes (upper dotted line) in the clusters. Finally, one can see from fig. 2 and the insert of fig. 3 that the probability of isostatic clusters is maximum in the window $\Delta \bar{r}$, and almost equal to 1 for the even SICA steps, providing evidence that the structure is almost stress-free.

Discussion. – Chalcogenide glasses represent the ideal systems to check these results. Different types of experimental measurements have given evidence of the two transitions and the nature of the self-organized intermediate phase. Raman scattering has been used [11, 13] as a probe to detect elastic thresholds in $\text{Si}_x \text{Se}_{1-x}$ and $\text{Ge}_x \text{Se}_{1-x}$ glasses. Specifically, changes in the CS mode chain frequencies have been studied with glass compositions and show a kink (or a jump) at the mean coordination number $\bar{r}_{c1} = 2.4$ and $\bar{r}_{c2} = 2.52$ in Ge- and $\bar{r}_{c2} = 2.54$ in Si-based systems, suggesting onset of a new rigidity at \bar{r}_{c2} . A clear correlation between these results and the vanishing of the non-reversing heat flow ΔH_{nr} (the part of the heat flow which is thermal history sensitive) in MDSC measurements has been shown [11, 13]. Obviously, since this ΔH_{nr} term provides a measure of how different a glass is from a liquid in a configurational sense, this suggests that in the intermediate phase, glass and liquid structure



Fig. 3 – Width of the transition $\Delta \bar{r}$ as a function of the fraction of MRO clusters at the rigidity transition for l = 2 (solid line), l = 3 (dashed line) and l = 4 (dotted lines). At step l = 2, the MRO clusters reduce to the edge-sharing GeSe_{4/2} tetrahedra. For larger steps, different rings sizes (4, 6, 8) have been taken into account. The lower dotted line corresponds to a system at l = 4 having only ES as MRO element. The insert shows the probability of isostatic clusters with mean coordination number \bar{r} for l = 4 (dotted line) and l = 3 (dashed line). The shaded region of l = 4 is defined by the corresponding $\Delta \bar{r}$.

are closely similar to each other.

The SICA and constraint-counting algorithms show that the width $\Delta \bar{r}$ of the intermediate phase increase with the fraction of ES tetrahedra and more generally with MRO composed of small rings (fig. 3). We stress that the width should converge to a lower limit value of $\Delta \bar{r}$ compared to the step l = 2, therefore one can observe the shift downwards when increasing lfrom 2 to 4. This limit value is in principle attained for $l \to \infty$, or at least for much larger steps than l = 4 [20]. For Si-Se, $\Delta \bar{r} = 0.14$ is somewhat larger than for Ge-Se ($\Delta \bar{r} = 0.12$) consistently with the fact that the number of ES is higher in the former [13].

In summary, we have shown that size-increasing cluster approximations could be used to go beyond the mean-field approach of the rigidity transitions. We have estimated for the different approximation steps the number of mechanical constraints and the number of floppy modes f and shown that two transitions were obtained in this situation: one at which fvanishes and another at which stressed rigid regions appear on the clusters. The width $\Delta \bar{r}$ is an increasing function of the MRO fraction. In the window $\Delta \bar{r}$, the rate of isostatic clusters is at its maximum. These new results should motivate developments on the role of local structure and MRO in the rigidity transition, and applications to Group-V chalcogenides such as $As_x Se_{1-x}$ glasses.

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