Understanding amorphous phase-change materials from the viewpoint of Maxwell rigidity

M. Micoulaut$^1$, J.-Y. Raty$^2$, C. Otjacques$^2$ and C. Bichara$^3$

$^1$ Laboratoire de Physique Théorique de la Matière Condensée, Université Pierre et Marie Curie, Boîte 121, 4, Place Jussieu, 75252 Paris Cedex 05, France
$^2$ Physique de la Matière Condensée, B5, Université de Liège B4000 Sart-Tilman, Belgium
$^3$ Centre Interdisciplinaire de Nanoscience de Marseille, CNRS et Universités d’Aix-Marseille, Campus de Luminy, Case 913, 13288 Marseille, France

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Phase-change materials (PCMs) are the subject of considerable interest because they have been recognized as potential active layers for next-generation non-volatile memory devices, known as Phase Change Random Access Memories (PRAMs). By analyzing First Principles Molecular Dynamics simulations we develop a new method for the enumeration of mechanical constraints in the amorphous phase and show that the phase diagram of the most popular system (Ge-Sb-Te) can be split into two compositional regions having a well-defined mechanical character: a Tellurium rich flexible phase, and a stressed rigid phase that encompasses the known PCMs. This sound atomic scale insight should open new avenues for the understanding of PCMs and other complex amorphous materials from the viewpoint of rigidity.

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Driven by applications in data storage$^1$, fundamental and applied studies of tellurides are rapidly developing. The most promising phase-change materials (PCMs) belong to the ternary Ge-Sb-Te system with particular compositions such as the Ge$_2$Sb$_2$Te$_5$ already used in industrial products$^2$. To optimize the peculiar property portfolio of these PCMs, a key issue is the understanding of their atomic structure. This has led to a series of investigations of the structure of both amorphous and crystalline phases using experimental as well as computer simulation techniques (for a review, see$^1$).

Since they are related to the ageing of PCMs$^3$, the mechanical properties of the amorphous phase are of major interest. In parent systems where the S-N rule holds (N: number of s and p electrons), particularly sulphur and selenium based amorphous networks, rigidity theory offers a practical computational scheme using topology, namely the Maxwell counting procedure, and has been central to many contemporary investigations on non-crystalline solids$^4,5$. It has led to the recognition of a rigidity transition$^5$ which separates flexible glasses, having internal degrees of freedom that allow for local deformations, from stressed rigid glasses which are "locked" by their high bond connectivity.

What happens if these elements are replaced by the heavier element Te which will lead to more complicated local structures, as highlighted both from experiments$^6,7$ and simulations$^3,8,9,10$? Does the counting procedure still hold? Attempts in this direction have been made on a heuristic basis$^8$, but they seem to contrast with experimental observations. A firm basis for the Maxwell constraint counting is therefore very much desirable to assess algorithms specially designed for PCMs. This is the purpose of the present study that develops a precise enumeration algorithm for constraints arising from bond-stretching (BS) and bond-bending (BB) interactions, based on the analysis of atomic scale trajectories using First Principles Molecular Dynamics Simulations (FPMD). Combined with rigidity theory, it opens an interesting perspective to study amorphous phase change materials in much the same fashion as network glasses. As a result, we show that the phase diagram of the Ge-Sb-Te system can be separated into two compositional regions having a well-defined mechanical character derived from rigidity theory: a flexible Te-rich phase, and a (Sb,Ge)-rich phase that is stressed rigid. The most commonly used GST phase change materials belong to this second category.

At the heart of the rigidity concept is the identification of relevant interatomic forces between atoms in a manner similar to what Maxwell pioneered for trusses and macroscopic structures$^{11}$. When applied to covalent amorphous networks and once the forces acting as constraints are identified (BS and BB forces), a similar analysis can be performed leading to the Phillips-Thorpe rigidity transition$^8$, which separates flexible (underconstrained) networks from stressed rigid (overconstrained) networks$^3,4$. As in standard mechanics however, instead of treating forces and querying about motion, one can ask the opposite question and try to relate motion to the absence of a restoring force. Using FPMD, we generate therefore atomic scale trajectories of various amorphous systems at low temperature using an electronic structure model (see$^{12,13}$ and EPAPS supplementary material for simulation details) and apply a structural analysis in relation with rigidity theory. The number of neighbors, and hence the number of BS constraints, is calculated by integrating the radial distribution functions up to its first minimum (Table I). To estimate the number of bond-bending constraints we analyze the partial
FIG. 1: (color online) a) Ge-centered bond angle distributions (up to 15) for various triplets of atoms $i0j$ ($i=1..6$, $j=2..5$) in amorphous GeSe$_2$. The six colored distributions have a low second moment (typically 10-20°, see panel b). The angle number assignments (1..15) displayed in the Ge panel are valid for all other angular studies. b) Second moment $\sigma_\theta ij$ of the distributions as a function of the angle number in amorphous GeSe$_2$: Ge-red and Se-centered angles (blue).

For each type of central atom 0, the six first neighbors $i$ are selected and sorted according to their distances, as done in [14], and the distributions $P(\theta_{ij})$ of the 15 corresponding angles $i0j$ ($i=1..5$, $j=2..6$) are calculated, i.e. 102, 103, 203, etc. The second moment $\sigma_\theta ij$ of $P(\theta_{ij})$ provides a quantitative estimate of the angular excursion around the mean value of angle $i0j$, thus measuring the strength of the bond-bending restoring force. An angle displaying a wide $\sigma_\theta ij$ corresponds to a broken BB constraint as there is a weak interaction to maintain the angle fixed. In an opposite way, sharp bond angle distributions lead to intact constraints.

In order to check this method, we first apply it to the benchmark case GeSe$_2$, for which application of constraint counting algorithms is straightforward [3]. According to the Phillips-Thorpe enumeration, one has for a $r$-coordinated atom respectively $r/2$ and $2r$-3 BS and BB constraints. Thus a four-fold Ge atom has 2 BS and 5 BB constraints whereas the two-fold selenium atom has 1 BS and 1 BB constraint leading on the overall to $n_c = 3.67$ constraints per atom [3]. We obtain the coordination numbers $r_{Ge}=4.04$ and $r_{Se}=1.98$ from the area of the first peak of the Ge- and Se-centered pair distribution functions. We furthermore find that $\sigma_\theta ij$ can vary between 10° and 40° depending on the different angles $i0j$ considered (Fig. 1). For the Ge-centered atoms, six moments $\sigma_\theta ij$ are found to be of the order of 10-20°, very well separated from all others for which $\sigma_\theta ij \simeq 40°$. However there is one redundant constraint that needs to be removed because it can be determined from the five other angles. This leaves the estimate with 5 independent BB constraints for the Ge atom. For the Se atom, a single low $\sigma_\theta ij$ (i.e. a single BB constraint) is found (12°) around the mean value $\theta_{ij} = 100°$, in agreement with experiment [15]. We arrive to the conclusion that the constraint computation from FPMD matches exactly the direct counting from [3].

Having validated the method with GeSe$_2$, we now turn to the amorphous Ge-Sb-Te system and focus on seven particular compositions, namely Ge$_{1-x}$Sb$_x$Te$_4$ (124), Ge$_2$Sb$_2$Te$_5$ (225), GeTe (101), GeTe$_6$ (106), GeSb$_6$ (160), Sb$_2$Te (021) and Sb$_2$Te$_3$ (023) (see also Fig. 4), using extensive FPMD simulations. We determine the BS constraints from the coordination numbers extracted from the partials (Table I). The coordination number of Ge and Sb is nearly equal to $r=4$, with a preference for heteropolar bonding with Te atoms, which have a coordination number between 2.1 and 2.9, larger than the 8-N value ($r=2$).
ing to the determination of corresponding BB constraints 
ond moments
ons. Fig. 3 shows the 15 different sec-
are displayed in Fig. 2. Certain angles clearly display a
σ
second moments are of the order of
bors are considered.
creased orientational disorder when more distant neigh-
large angle number \( n \) (i.e. \( n > 6 \)), which suggests an
increased orientational disorder when more distant neigh-
bor are considered.

In the ternary compositions 124 and 225, only three
second moments are of the order of \( \sigma_{ij} \approx 10-15^\circ \)
for the Ge and Sb atoms, associated with well-defined angles at \( \theta_{ij}=90-100^\circ \) which are, together with those found at
\( \approx 180^\circ \), reminiscent of the distorted octahedral-like rock-
salt cubic phase \([6,10]\). The present results contrast with the view that would follow the standard enumeration of
constraints, directly derived from coordination numbers
obeying the 8-N rule. In fact, a three-fold Sb would give
rise to 1.5 BS and 3 BB constraints \([5]\). Here, Sb has
an additional neighbor that increases the number of BS
constraints but it does not give rise to two additional BB
constraints (Fig. 3).

Although it is found \( r_{Te} > 2 \), Te has only one angular
constraint (Fig. 3, \( \sigma_{ij}=12^\circ \) in the 124 and \( \theta_{ij} \approx 95^\circ \)),
the two other possible angles (angle number 2: 103 and
6: 203) being much more flexible (\( \sigma_{ij}=27^\circ \) and \( 29^\circ \)). On
the basis of this enumeration, and using results of Table
I and of Fig. 3, a Maxwell estimate for the number of BS
and BB constraints of Ge\(_x\)Sb\(_y\)Te\(_{1-x-y}\) is given by :

\[
\begin{align*}
    n_c & = \frac{1}{2} \left[ x(r_{Ge} - r_{Tc}) + y(r_{Sb} - r_{Tc}) + r_{Tc} \right] \\
    & + \left[ x(n_{Ge}^{BB} - n_{Tc}^{BB}) + y(n_{Sb}^{BB} - n_{Tc}^{BB}) + n_{Tc}^{BB} \right]
\end{align*}
\]

where the square brackets are used to separate BS from
BB contributions. Results for the seven compositions are
given in Table I. They furthermore take into account the
possibility of two local environments for four-fold Ge
in the presence of Te also found in \([8,9]\): a majority of dis-
torted octahedral sites having 3 constraints for the angles
\( \theta_{ij}=90-100^\circ \) (see Fig. 3), and a minority of tetrahedral
Ge (calculated to have a respective fraction of \( \eta = 0.1 \)
and \( \eta = 0.2 \) in the 225 and 124) which have 5 BB constraints
as in GeSe\(_2\). This means that the average number of Ge
BB constraints is \( n_{Ge}^{BB} = 5\eta + 3(1-\eta) = 3 + 2\eta \) and leads
finally to \( n_{c}^{124}=3.59 \) and \( n_{c}^{225}=3.47 \), \( r_{Tc} \) being calculated
for each composition using Table I. One can thus con-
de that 124 and 225 are stressed rigid, i.e. they have
more constraints than degrees of freedom (3 in 3D).

\begin{table}
\begin{center}
\begin{tabular}{|c|c|c|c|}
\hline
Compound & Atom & \( r_i \) & \( n_i^{BB} \) & \( n_c \) \\
\hline
GeTe\(_6\) & Ge & 4.0 & 3.3 & \\
& Te & 2.4 & 1.0 & 2.68 \\
\hline
GeTe & Ge & 4.1 & 3.0 & \\
& Te & 2.9 & 1.0 & 3.75 \\
\hline
Ge\(_2\)Sb\(_2\)Te\(_4\) & Ge & 4.0 & 3.4 & \\
& Sb & 4.1 & 3.0 & \\
& Te & 2.8 & 1.0 & 3.59 \\
\hline
Ge\(_2\)Sb\(_2\)Te\(_5\) & Ge & 4.0 & 3.2 & \\
& Sb & 3.8 & 3.0 & \\
& Te & 2.4 & 1.0 & 3.47 \\
\hline
GeSb\(_6\) & Ge & 4.1 & 5.0 & \\
& Sb & 3.7 & 3.0 & 5.16 \\
\hline
Sb\(_2\)Te & Sb & 4.0 & 3.0 & \\
& Te & 2.5 & 1.0 & 4.08 \\
\hline
Sb\(_2\)Te\(_3\) & Sb & 3.7 & 3.0 & \\
& Te & 2.1 & 1.0 & 3.17 \\
\hline
\end{tabular}
\end{center}
\caption{Coordination number \( r_i \) of the atomic species, giving
the number of bond-stretching (BS) constraints \( (r_i/2) \),
number of BB constraints \( n_i^{BB} \) computed from the second
moments of the bond angle distributions \( P(\theta_{ij}) \), and
total number of constraints \( n_c \) in the seven different Ge-Sb-Te
compounds.}
\end{table}
Tetrahedral networks are known to be a fundamental feature of amorphous materials, and their number of neighbors can be used to determine rigidity. In the case of germanium antimony telluride (GeSbTe), the system is known to have tetrahedral sites, where each Ge or Sb atom has four neighbors. In an amorphous phase, this rigidity is lost due to the stress and flexibility of the network.

The relationship (2) is found to be close to the composition $y = \frac{7}{27 + 20x} - x$.

In summary, we have developed a new constraint counting algorithm applicable to tellurides for which a simple counting based on the 8-N rule does not apply in a straightforward manner. We show that atomic-scale trajectories obtained from First Principles Molecular Dynamics simulations can be appropriately used for the estimation of bond-stretching and bond-bending constraint counting and applied to the GST phase-change system. The results show that amorphous systems lying on the popular Sb$_2$Te$_3$-GeTe tie-line in the GST compositional triangle belong to stressed rigid phase, whereas an rigidity transition line is obtained close to the SbTe$_4$-GeTe$_4$ join. Furthermore, since an intermediate phase with some remarkable properties (absence of ageing, stress-free character and space-filling tendencies) has been found close to $n_c = 3$ in sulphide and selenide systems, one may wonder to what extent these properties can be observed in tellurides as well, and how these properties, once being observed, could be used in close future to design phase-change materials with the corresponding functionality.

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