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# *Ab initio* molecular dynamics study of GeS<sub>2</sub>: from the crystal to the glass

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## Abstract

Using density-functional molecular dynamics simulations we analysed the different steps that permit us to create a glass starting from a crystal in the case of GeS<sub>2</sub>. Thus we studied, mainly from a structural point of view,  $\alpha$ -GeS<sub>2</sub> crystals, GeS<sub>2</sub> liquid at 2000 K and the evolution of the system during the quench. We found that in the liquid a first sharp diffraction peak exists even though the atoms are in a diffusive state. During the quench we evaluated the lifetime of the different interatomic bonds and we showed that the 'wrong' bonds present in the liquid can be destroyed and re-created several times during the length of the quench. Thus the ultra-fast cooling rates used in simulations cannot solely be held responsible for the structural differences that may be found between experimental and simulated glasses.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

During the workshop 'Nanoscale order in amorphous and partially ordered solids' several presentations have been devoted to the properties of chalcogenide glasses because they offer a wide range of applications such as optical amplifiers, memory switching devices or anti-reflection coatings [1] and are thus the topic of intensive research (see the other contributions in these proceedings).

Among the different research means, molecular dynamics (MD) simulations can be a very interesting tool to provide detailed information on the physical properties of such glassy systems. Firstly because they allow us to investigate the structure in full microscopic detail, giving access to the position of the atoms and, secondly, because they are useful to study dynamical phenomena accessible to such simulations, e.g. for timescales between  $10^{-13}$  and  $10^{-8}$  s.

Nevertheless the problem one is confronted with in MD simulations is the way the glassy samples are prepared and in particular the timescales used to bring the system from the crystal to the glass during a standard 'cook and quench' procedure. This procedure is supposed to

mimic the experimental way to make a glass but, due to the limited amount of computer time, the whole building process is  $10^{12}$ – $10^{14}$  times faster than in ‘real life’. In this work we want to show, mainly from a structural point of view, how the properties of a germanium disulfide sample change when going from the  $\alpha$ -GeS<sub>2</sub> crystalline state to the glass. The paper is consequently organized as follows. In section 2 we briefly present the theoretical model used in our calculations. Results and discussions are presented in section 3 for the crystalline, liquid and cooling phase. Finally, in section 4 we summarize the major conclusions of our work.

## 2. Theoretical framework

Computations were performed using Fireball96, an approximate *ab initio* molecular dynamics code based on the local-orbital electronic structure method developed by Sankey and Niklewski [2]. The electronic structure is described using density-functional theory (DFT) [3] within the local density approximation (LDA) [4] and the non-local pseudo-potential scheme of Bachelet *et al* [5]. To reduce the CPU time, we used the non-self-consistent Harris functional [6] with a set of four atomic orbitals (1 ‘s’ and 3 ‘p’) per atom that vanish outside a cutoff radius of  $5a_0$  (2.645 Å). This model has been successfully used over the last ten years for several different chalcogenide systems [7–9].

All the calculations of the present simulations were performed in the microcanonical ensemble, with a time step  $\Delta t = 2.5$  fs and using only the  $\Gamma$  point to sample the Brillouin zone.

## 3. Results

### 3.1. The $\alpha$ -GeS<sub>2</sub> crystal

We start our simulations from an  $\alpha$ -GeS<sub>2</sub> crystalline sample containing 258 particles in a cubic box of 19.21 Å, which corresponds to an experimental density of 2.73 g cm<sup>-3</sup> [10], and we apply the standard periodic boundary conditions. In order to compare the static structure factor  $S(q)$  of the crystal to that of the liquid and the glass, we let first this  $\alpha$ -GeS<sub>2</sub> crystalline sample evolve at 300 K for 5 ps which permits us to obtain the  $S(q)$  (figure 1) taking into account the thermal motion of the atoms which corresponds to the structure factor that could be measured experimentally for a crystal at room temperature. From figure 1 we can determine the presence of a first sharp diffraction peak (FSDP) in  $S(q)$  at  $\approx 0.88 \text{ \AA}^{-1}$  which corresponds to a distance in real space of  $\approx 7.2 \text{ \AA}$ . This distance corresponds to the interlayer distance between the 2D layers that make up the  $\alpha$ -GeS<sub>2</sub> crystal (figure 2). These layers act like Bragg planes and are at the origin of the peak at  $\approx 0.88 \text{ \AA}^{-1}$  and this is also confirmed when looking at the partial structure factors which indicate that all interatomic pairs contribute equally to this peak.

### 3.2. The GeS<sub>2</sub> liquid

The next step in our process of making the glass is to melt the crystal. In experimental studies this is done at a temperature slightly higher than the experimental glass transition temperature ( $T_g \approx 720 \text{ K}$  [10]) but since the simulation times are relatively limited in MD studies one needs to obtain an equilibrated liquid in a relatively short amount of time and that is why our  $\alpha$ -GeS<sub>2</sub> crystalline sample has been melted at 2000 K for 60 ps. During this period one can measure the root mean square displacement (MSD) of the Ge and the S atoms and the result is depicted in figure 3. The slope of the MSD is close to 1 which indicates that, as expected, the atoms diffuse in the liquid. The slope becomes exactly equal to 1 at the end of the simulation time and thus

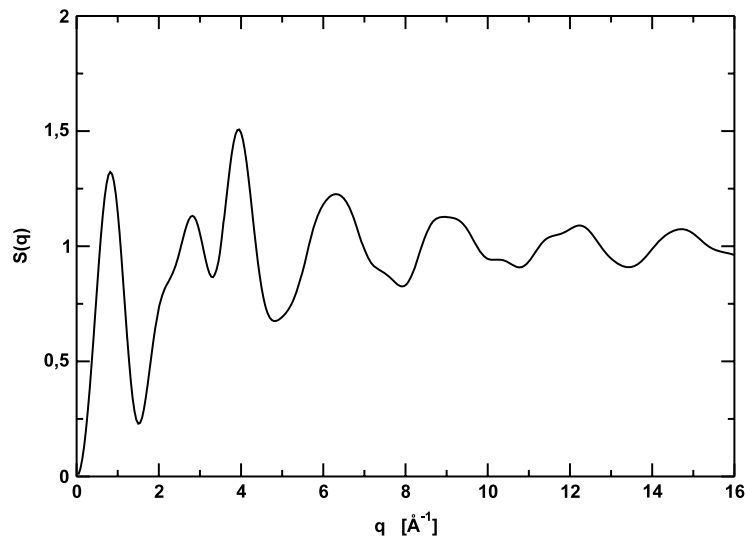


Figure 1. Structure factor of the  $\alpha$ -GeS<sub>2</sub> crystal at 300 K.

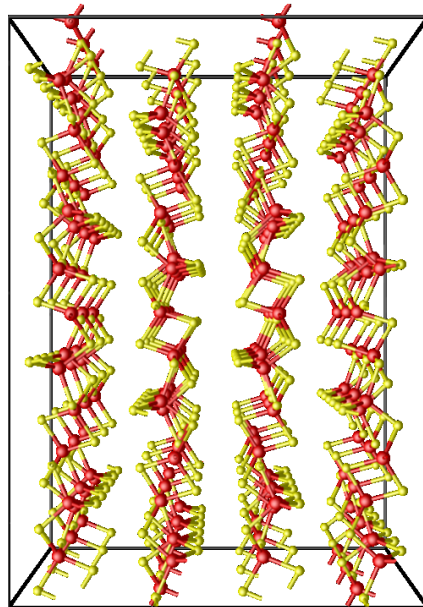
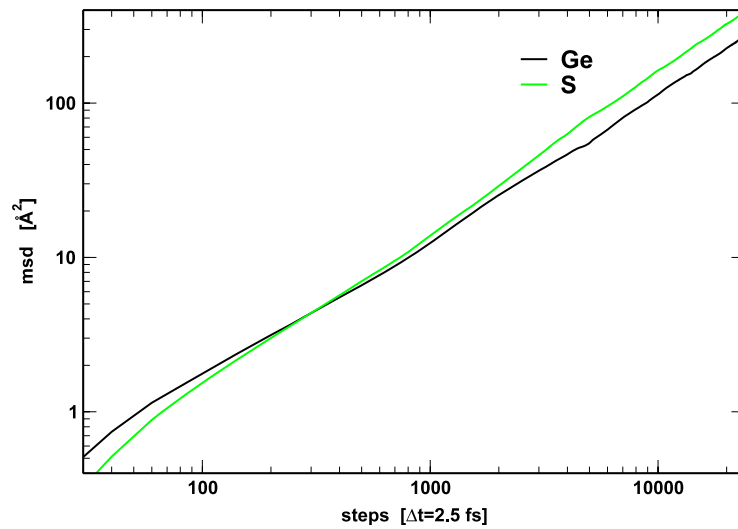
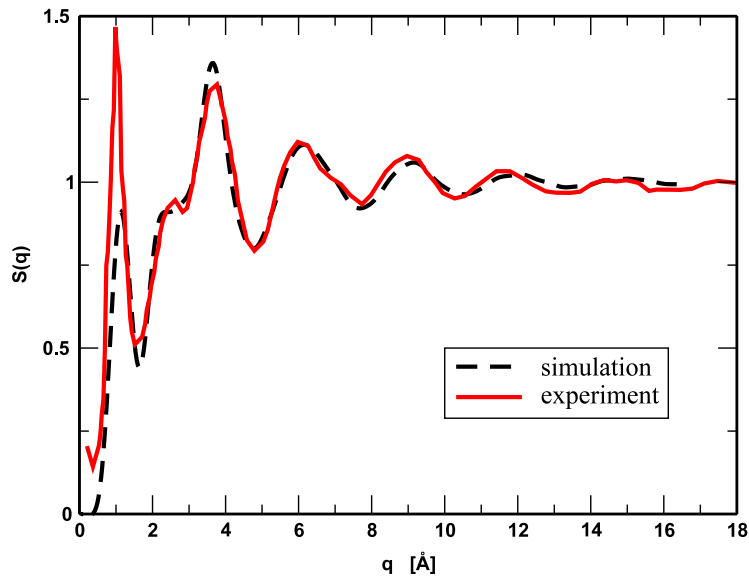


Figure 2. Snapshot of the layered structure of the  $\alpha$ -GeS<sub>2</sub> crystal.

we can extract the diffusion coefficient of the Ge atoms ( $7.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) and the S atoms ( $1.07 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ ) at 2000 K. From figure 3 one can determine that the Ge atoms travelled on average 15 Å with respect to their initial crystalline position while the S atoms travelled on average 20 Å, which indicates that the initial crystalline structure has really been wiped out. To check this important statement we have calculated the structure factor of the GeS<sub>2</sub> liquid on 40 additional ps and the result is shown in figure 4 together with the experimental structure factor obtained at  $\approx 1300 \text{ K}$  [11]. We see that a FSDP is also present in the liquid even

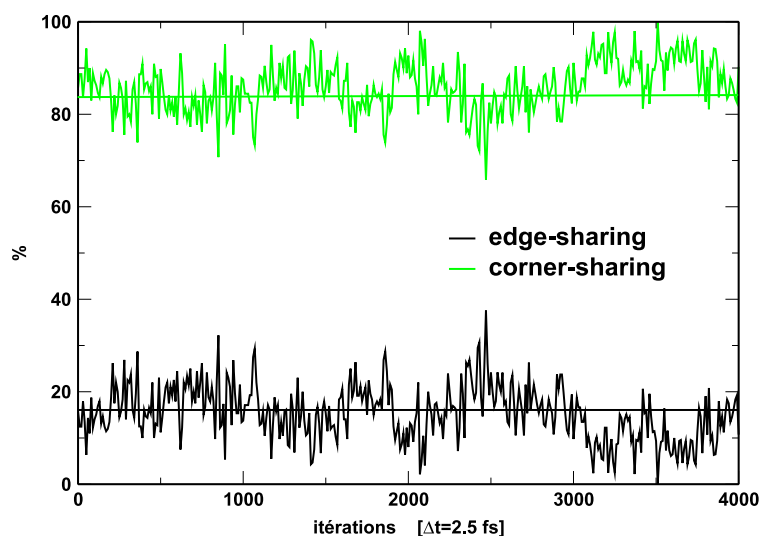


**Figure 3.** Mean square displacement of the Ge and S atoms at 2000 K starting from the crystalline configuration.



**Figure 4.** Structure factor of simulated liquid  $\text{GeSe}_2$  at 2000 K compared to the experimental  $S(q)$  obtained at  $\approx 1300$  K.

though its position has shifted to a slightly higher  $q$  value ( $\approx 1.1 \text{ \AA}^{-1}$ ). Such a shift has also been observed in other chalcogenide systems such as  $\text{GeSe}_2$  [12]. It is interesting to note that at 2000 K no periodic arrangement of quasi-Bragg planes is conceivable in the liquid, which is in contradiction with the proposition of Gaskell *et al* who claim that the FSDP is due to the existence of quasi-Bragg planes in the amorphous phase [13]. When we evaluate  $S(q)$  from *one* liquid configuration we note that the intensity and the position of the FSDP varies depending on the configuration chosen. This has also been observed in  $\text{GeSe}_2$  glasses by Massobrio *et al*

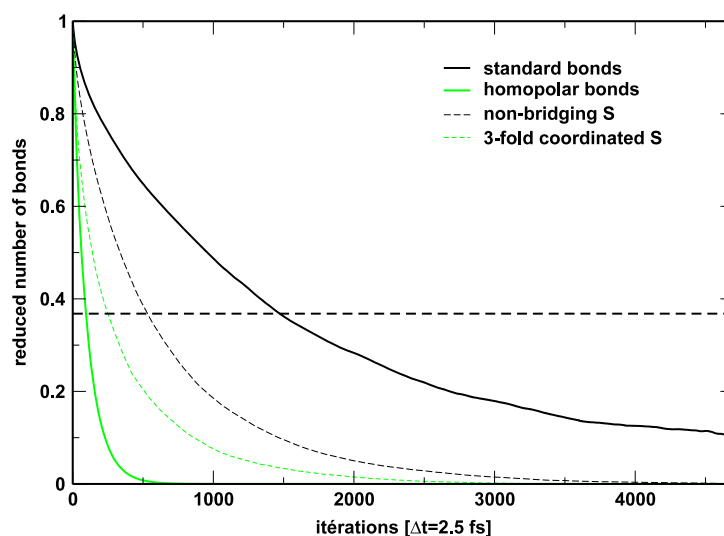


**Figure 5.** Proportion of edge and corner sharing bonds in the liquid at 2000 K versus time.

[14] and indicates that the liquid sample used to build the glass has to be chosen with great care. The modification of the medium range order all along the melt can also be observed by monitoring the evolution of the proportion of corner and edge sharing bonds in the liquid sample (figure 5). These proportions fluctuate around the values found experimentally [15] and theoretically [7] in the  $\text{GeS}_2$  glass (represented by the horizontal lines in figure 5) which therefore appear as equilibrium values for the connectivity of amorphous  $\text{GeS}_2$ . We could not link directly the variations in the connectivity of the network to the intensity and the position of the FSDP, but it appears that the liquid configurations with a proportion of corner and edge sharing links particularly different from the equilibrium values obtained in the glass show a FSDP particularly different from the one measured in glassy  $\text{GeS}_2$ .

### 3.3. From the liquid to the glass

In MD simulations, the way the liquid sample is cooled down to room temperature (or lower temperatures) is extremely rapid and can therefore affect the properties of the resulting glass since it has been shown both experimentally [16] and theoretically [17] that the characteristics of the glass depend on its thermal history. We have recently shown how the quenching rate affects the properties of our  $\text{GeS}_2$  glasses cooled down to room temperature [18] with quenching rates ranging from 3 to  $0.06 \times 10^{14} \text{ K s}^{-1}$  and in particular we have found that the chemical disorder ('wrong bonds') does not really disappear for the lowest quenching rates. Therefore it is interesting to analyse the bonding defects (homopolar bonds, over- or under-coordinated atoms) present in the liquid and to check if they are 'frozen in' during the ultra-fast quench without having the time to be eventually destroyed. To that aim we study the lifetime of the bonds in the first steps of the fastest cooling rate we have used to build our glasses:  $6 \times 10^{14} \text{ K s}^{-1}$ . We calculate the reduced number of bonds present at time  $t = 0$  (in the liquid) and that are still present at time  $t$ . This quantity is then auto-correlated over 500 configurations in order to average the data and the results are presented in figure 6. We distinguish the standard bonds (a Ge atom bonded to four S atoms, a S atom bonded to two Ge atoms) from the 'wrong' bonds (homopolar bonds, non-bridging sulfur atoms, over-coordinated S atoms). The curves



**Figure 6.** Lifetime of the different bonds during the first steps of a quench.

in figure 6 can be fitted with  $\exp(-\alpha t)$  functions where  $\alpha$  is the inverse of a characteristic time. This characteristic time, which represents the ‘lifetime’ of a given bond, can be estimated in figure 6 by determining the time corresponding to a value of  $y = 1/e$  (horizontal dashed line) on each curve. This way we evaluate the lifetime for each type of bond and we find that the wrong bonds have a much shorter lifetime than the standard bonds (3.7 ps (1480 iterations)). The non-bridging sulfur atoms survive on average 1.32 ps (530 iterations), the three-fold coordinated S atoms survive on average 0.6 ps (252 iterations) and the S–S and Ge–Ge homopolar bonds have an extremely short lifetime of 0.22 ps. These extremely small values indicate that the bonding defects present in the liquid are not frozen in during our simulated quenches that last for at least 5 ps for the fastest rate and more than 500 ps for quenches close to  $10^{12} \text{ K s}^{-1}$ . Thus we determine that the bonding defects (and in particular homopolar bonds) have the time to be destroyed and then recreated with other atoms a great number of times (up to 500 times) during the time of the quench. Hence atoms in an energetically unfavourable environment in the liquid are not trapped by the rapid decrease of the temperature and can reach an energy minimum with much destruction and creation of bonds. The properties of the so-obtained glass have been thoroughly studied [7, 8] and presented during this workshop. The results compare well with experimental data (when available) concerning the structural, vibrational and electronic aspect and this shows, together with the results presented in this work, that the ultrafast quenching rates used in simulations cannot be held responsible for the differences between the ‘real’ glass and the simulated glass, at least not for the vast majority of them.

#### 4. Conclusion

Through DFT based molecular dynamics simulations we have analysed the process used to build a simulated  $\text{GeS}_2$  glass by studying the initial  $\alpha\text{-GeS}_2$  crystal structure, the liquid at 2000 K and finally the evolution of some structural defects during the quench. Concerning the first sharp diffraction peak in the static structure factor we have shown that it is already present in the liquid while in the crystal the first peak corresponds to the periodic arrangement of the 2D

layers present in the  $\alpha$  form of the GeS<sub>2</sub> crystal. The medium range order in the liquid (height and position of the FSDP, proportion of corner and edge sharing bonds) fluctuates around the values found in the glass and therefore the initial liquid structures used for the quench should be chosen carefully. We show that during the computer quench the ‘wrong’ bonds present in the liquid have time to be destroyed and re-created a great number of times before the system reaches 300 K, which indicates that the ultra-fast cooling rates (up to  $10^{14}$  K s<sup>-1</sup>) used in simulations due to the high CPU time requirements especially needed in *ab initio* simulations should not be used as the principal argument to explain some of the differences that may be found between the experimental glass and the simulated glass, differences which are minor concerning the case of GeS<sub>2</sub> systems as we have shown in previous studies [7, 8].

Obviously the slower the cooling rate, the better the glass. But the results show that one should not be focused on this aspect of the building process of the simulated glass since even results obtained with rates as fast as  $10^{14}$  K s<sup>-1</sup> are in good agreement with experimental data. Nevertheless we have recently shown that one should not cool a liquid too fast [18] if one wants to obtain a glass and not a frozen liquid. This ‘critical’ quenching rate probably exists for all the systems but its value will depend on the composition and the theoretical model used to describe the different elements present in the glass.

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