

# Simulations of arsenic selenide glasses

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## Abstract

In this paper we make some general comments on the methods used for modelling glasses and use glassy GeSe<sub>2</sub> as an example. We then emphasize recent work on As–Se glasses, including glassy As<sub>2</sub>Se<sub>3</sub> and amorphous AsSe. The topology and electronic and vibrational properties of the models are discussed and with their use we infer the microscopic nature of the valence band x-ray photoemission (XPS) signal of g-As<sub>2</sub>Se<sub>3</sub> and AsSe. We note that the XPS signal may be interpreted as arising from three distinct subbands with well defined structural origins.

## 1. Introduction

Arsenic selenide glasses are among the most important of the glassy chalcogenide materials. The stoichiometric composition As<sub>2</sub>Se<sub>3</sub> is a classic glass former and also has the interesting feature of having a composition exactly at the floppy-to-rigid transition [1] (with mean coordination  $\langle r \rangle = 2.4$ ). The composition AsSe has special interest because of the opto-mechanical effect [2] (the only known direct mechanical signature of the polarization of light). In this paper, we discuss models of these glasses and comment on their topology and electronic and vibrational properties. We also discuss some generic aspects of modelling disordered materials including As–Se glasses. These networks may be used as a starting point for other studies, such as modelling photo-structural response [3].

## 2. General remarks on modelling amorphous materials

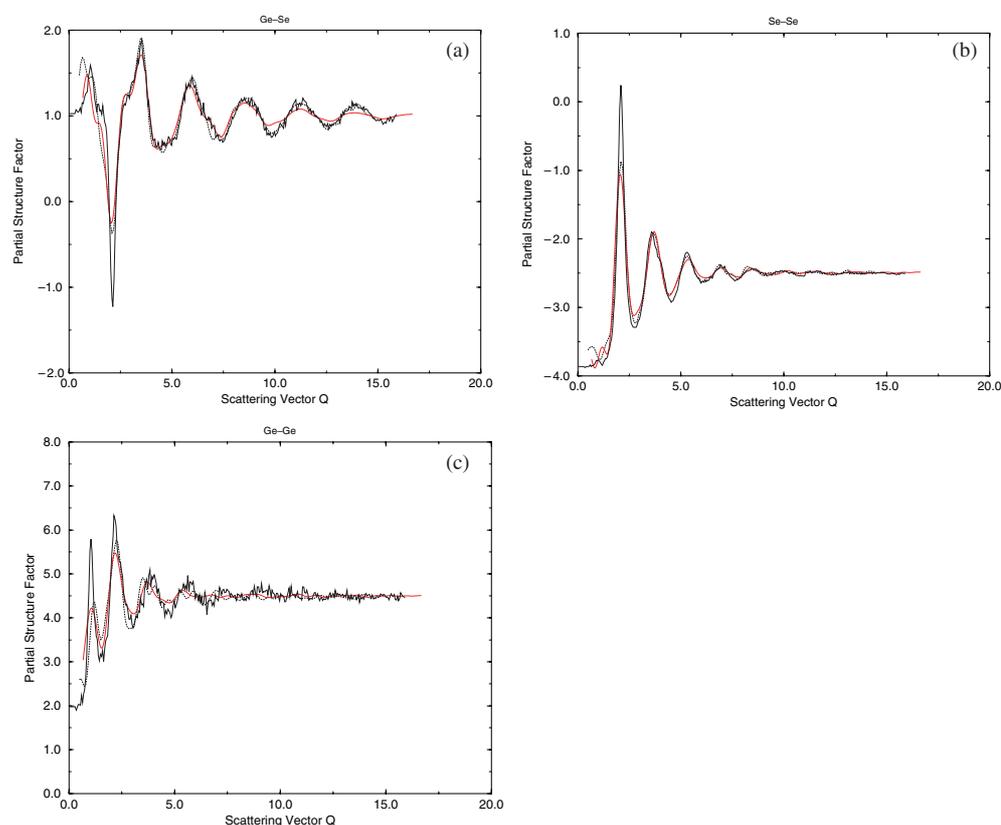
We have empirically found that a simple simulation regime (a molecular dynamics (MD) quench from the melt) can work quite well for As–Se glasses with a suitably simplified *ab initio* density functional Hamiltonian. We often refer rather irreverently to a quench from the melt technique as ‘cook and quench’. This scheme *cannot* be expected to work for general amorphous systems [4]. We have conducted studies on a variety of Se alloy glasses which have convinced us that it is relatively easy to construct realistic models (meaning in adequate agreement with experiment) for stoichiometric compositions (such as As<sub>2</sub>Se<sub>3</sub> or GeSe<sub>2</sub>), but that it is much more challenging to construct models at compositions far from stoichiometry. Almost certainly, the ease of constructing quality models at these special compositions is

connected to the *physical* glass forming process. In microscopic terms, this is connected to the similarity of the topological (and chemical) order in the liquid, not far above the melting point, and the glass. From a naive point of view this is altogether remarkable, since the timescale of quenching materials in the laboratory is dramatically longer than the timescale that we simulate on the computer.

Unexpected difficulties in model making can also arise in materials often supposed to be 'simple'. Beyond doubt, amorphous Si (a-Si) is the most studied disordered material. Yet 'cook and quench' does a rather poor job of providing models [5a] which is initially puzzling, since *ab initio* methods accurately represent the relevant part of the Si phase diagram. This by itself is clearly not, however, a guarantee that computer melt quenching will result in a realistic physical model. There are at least two key limitations to these simulations: timescales (radically shorter in the simulation) and length scales (many simulations have been carried out for 64-atom cells and are significantly strained). We note that one cannot even make respectable a-Si in the laboratory by melt quenching: microcrystalline muck is the product of such experiments. One supposes that the problem for the simulation (and perhaps Nature in this case!) is that MD simulations simply cannot unravel all the changes in topology necessary to faithfully model the amorphous solid state which is so topologically different from the sixfold-coordinated liquid. Fortunately, alternative methods based on the Wooten–Weaire–Winer (WWW) [6] bond-switching approach and Keating springs are brilliantly successful for a-Si. We suppose that the efficacy of this scheme originates in its imposition of the constraint of fourfold coordination for Si (an excellent approximation and a fine example of the use of *a priori* information in model building).

The remarks of this section are largely independent of the choice of energy functional used. In some cases simple analytic potentials can succeed very well; in certain cases very high-accuracy calculations can be needed. However, the simulation regime (in the sense of the cooking, quenching, and 'annealing' processes) should be optimized for whatever energy functional is chosen. Any MD approach suffers to varying degrees from the 'timescale problem' (unphysically rapid quench times in comparison with experiment). If one tries to anneal a model, virtually all of the MD steps consist of 'oscillating in a harmonic (or nearly harmonic) well', which provides no information about the energy landscape away from the minimum. One can instead go to very high temperatures (quite near the melting point) to force the emergence of 'more interesting' events, but the question arises as to whether these are the same events as are seen (rarely) at lower temperatures. A development of great importance is recent work designed to enable access to a much larger part of the configuration space. A method which has been applied to amorphous systems is the 'activation–relaxation technique' (ART) of Barkema and Mousseau [7]. In this scheme, one 'hunts' quite efficiently for saddles connecting basins of different energy minima, and one can explore dynamical events which occur on timescales vastly longer than the picosecond times of common MD simulations. Such calculations are also ideal for modelling diffusive phenomena (such as ion motion in a glassy host), and we expect significant advances to accrue from such studies.

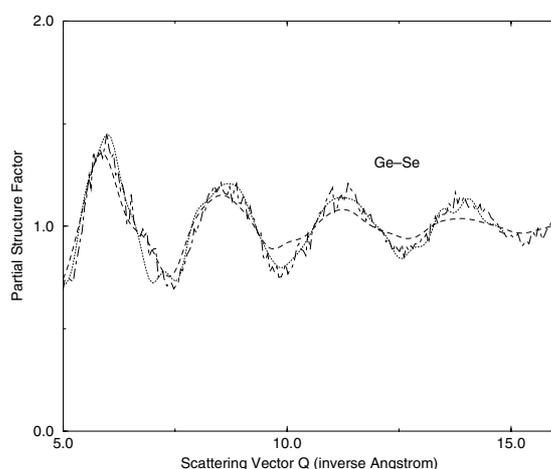
To illustrate the applicability of alternatives, reflect on the limitations of the quench from the melt procedure, and demonstrate the utility of providing *a priori* information in a starting model, we give an example. While the calculation of this paragraph involves GeSe<sub>2</sub> rather than an As–Se glass, we believe that the discussion has rather generic interest. We made a model of g-GeSe<sub>2</sub> by starting with a defect-free (fourfold-coordinated) 64-atom supercell model of a-Ge made with the WWW method [6]. Characteristic of an amorphous column IV material, this model has bond angles tightly centred on the tetrahedral angle, and has a topology presumably unrelated to g-GeSe<sub>2</sub>. We decorated all of the Ge–Ge bonds with a bond-centred Se, and rescaled the coordinates to the experimental density of g-GeSe<sub>2</sub>. This 192-atom



**Figure 1.** Partial structure factors  $S(Q)$  for glassy  $\text{GeSe}_2$ . The solid curves are from experiment (see [8]), the dashed curves are from the ‘cook and quench’ model (see [9]), and the fine dotted curves are from the decorated WWW model (see the text). The units of the scattering vector  $Q$  are  $\text{\AA}^{-1}$ .

(This figure is in colour only in the electronic version)

model was then steepest-descent quenched with Fireball [10]. In figure 1, we illustrate the results for the partial static structure factors  $S(Q)$  from experiment [8], our prior model of g- $\text{GeSe}_2$  [9], and the new ‘decorated’ model. The new model is at least as good as the previous model and is comparable to the models of Massobrio and co-workers [11]. While the models have strong similarities, manifested in the partial structure factors, and essentially similar topological/chemical ordering, a key difference of the ‘decorated’ model is the persistence of oscillations in the Ge–Se  $S(Q)$  beyond  $10 \text{\AA}^{-1}$  in pleasing agreement with experiment, whereas the earlier model displays a more rapidly decaying amplitude for large  $Q$  (we illustrate this in figure 2). One may interpret this as implying that the ‘cook and quench’ model was too ‘liquid-like’—precisely the kind of artifact one might expect from rapidly quenching a liquid on the computer. As both models are based on the same interatomic interaction (Fireball [10]), this is clearly a comment about the *simulation regime*. The new model has 86% heteropolar bonds, 13.5% homopolar Se–Se bonds, and a single Ge–Ge bond (0.5%). Ge was 78% fourfold, 19% threefold, and 3% twofold coordinated, numbers quite consistent with our earlier model. We think that the plausibility of our ‘decorated’ model is an interesting result, since it was extremely ‘cheap’ to generate from a computational point of view. It is quite possible that the



**Figure 2.** A blow-up of the Ge-Ge partial structure factor for glassy  $\text{GeSe}_2$ . Note the rapid decay of  $S(Q)$  for the quenched model (see [9]) and improved agreement with experiment (see [8]) for the decorated WWW model. The curve styles are as in figure 1.

model could be improved further by a process of cook and quench *based upon the decorated model as an initial conformation*. We are investigating these issues, plus the electronic and vibrational properties of this model, and will report on them elsewhere.

An important general difficulty when comparing experiment and theory is the non-specificity of many easily computed or measured functions. The structural pair correlations (especially if restricted only to the total pair correlations) are notorious in this regard. To some degree electronic and vibrational spectra suffer in a similar way, at least for the smooth broadband part of the spectra. It would be an interesting exercise to *quantify* ‘information content’ for these spectra by computing the information entropy [12]  $S[\rho] = - \int d\omega \rho(\omega) \log \rho(\omega)$  for each spectrum  $\rho(\omega)$ . The entropy functional is of course a maximum (reflecting least information) for the smoothest curves, and smallest for delta functions (reflecting maximum information). For very smooth and broad experimental and theoretical curves it is of course possible that ‘agreement’ between experiment and theory confers little credibility on the significance of the model.

In this connection, localized (and therefore spectrally sharp and isolated) features in either the electronic or vibrational density of states (VDOS) can carry key information about defects or network irregularities. Thus, one of the best ways to infer that a model is unrealistic is to find a significant density of defect states for a material that actually has few such gap states. The logic is that such defects (appearing in a model but not the experiment) must be absent in the real material, thereby providing very specific local information about errors in the model. Gap states (which are inevitably spatially localized) provide information that is not to be found in a smooth continuum band. Many simulations, even of an *ab initio* type, do *not* report the density of electronic states. This information is required for the complete appraisal of a model.

On a final ‘generic’ note, we believe that the key point in modelling amorphous materials is *not* the simulation regime or the Hamiltonian used. The only point that matters in the end is whether a model, whatever its origins, agrees with *all the experimental information*. After all, no simulation can make a plausible claim to mimic the *physical* process of glass formation. The details required to obtain experimentally realistic models can vary dramatically depending on the material.

### 3. Arsenic selenide glasses

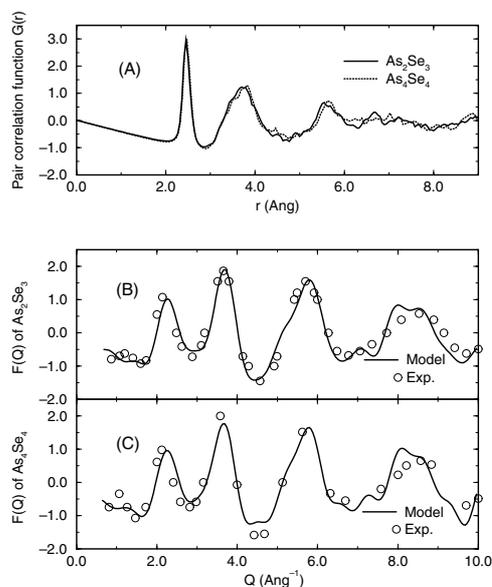
We found that the elementary ‘cook and quench’ approach was effective for  $\text{As}_2\text{Se}_3$  [13] and  $\text{AsSe}$  [14]. In particular, the total static structure factors for both materials are in agreement with the x-ray diffraction studies of Renninger and Averbach [15]. On a somewhat cautionary note, we observe that the total static structure factors for these glasses are remarkably close, despite some significant topological differences in the models, so one must not be too impressed by the pair correlations alone. On the other hand, the calculated electronic/optical properties seem to be quite good for both systems, which lends additional credence to the models.

In these simulations we used ‘Fireball’, a code developed by Sankey *et al* [10]. This is a fully *ab initio* approach to electronic structure, force, and dynamical simulation. It is also *approximate*, in the sense that while derived from density functional theory in the local density approximation, it employs additional approximations. These are:

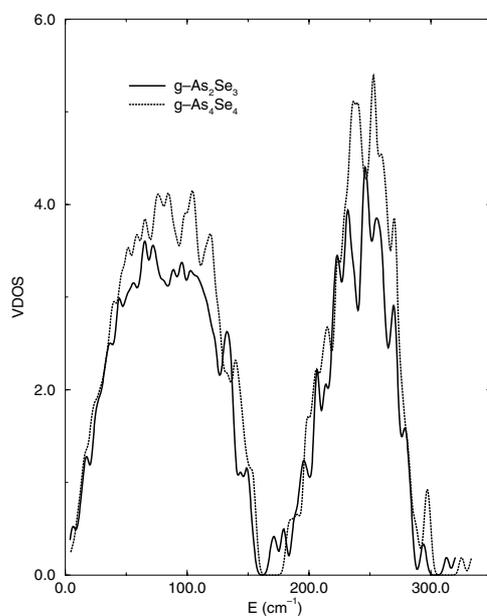
- (1) non-local, norm-conserving hard pseudopotentials;
- (2) a minimal (single-zeta) basis of one s and three p orbitals per site (these are selected to be slightly excited pseudoatomic orbitals);
- (3) the Harris functional as an alternative to self-consistent field iterations of the Kohn–Sham equations (for covalent or nearly covalent systems this is an excellent approximation for neutral atoms as ‘input density’)—the success of the Harris functional stems in part from the fact that it is a stationary principle (implying that errors in the energy are *second order* in the difference between the input and exact electron densities);
- (4) finally, physically motivated approximations are used for the multicentre matrix elements for the exchange–correlation matrix elements.

For the systems that we discuss here, and many others, this approach is accurate enough to produce excellent models of glasses at a small fraction of the cost of a self-consistent plane wave approach. It does not have some of the nice features of such calculations (like a ‘single knob’ to adjust the completeness of the basis), but where applicable it has been a very successful methodology. To form our models, we used 200–300-atom cells with the appropriate composition and the density of the glass. At constant volume throughout, we ‘melted’ the crystalline phases, equilibrated them for 2 ps at 2000 K, ‘cooled’ them to 700 K by velocity rescaling over a time of 4 ps, equilibrated the systems at 300 K for several picoseconds, and then performed several annealing cycles near the glass transition temperature until a satisfactory model was obtained. Obviously there is nothing unique about this ‘recipe’, but we found it to be highly effective for these glasses.

In figure 3, we illustrate the real-space pair correlation functions for both g- $\text{As}_2\text{Se}_3$  and a- $\text{AsSe}$ , and compare them with experiment [14]. The agreement between experiment and theory is quite good. The difference between the total pair distribution functions of the two glasses is surprisingly small and is most clearly seen in figure 3(A). These materials are readily understood as consisting of ‘building blocks’ (As–Se pyramids being predominant in  $\text{As}_2\text{Se}_3$ , and  $\text{Se}_2\text{As–AsSe}_2$  dominating in  $\text{AsSe}$ ). For  $\text{As}_2\text{Se}_3$  we find that 61% of the atoms are part of pyramids, the residue being mostly the  $\text{Se}_2\text{As–AsSe}_2$  structure. For  $\text{AsSe}$ , 70% of the atoms are part of the  $\text{Se}_2\text{As–AsSe}_2$ , with most of the remaining atoms being part of pyramids. Where the ‘8-N’ rule is concerned, we note that As is nearly always threefold-coordinated (96.5 and 98.4% threefold coordinated in  $\text{As}_2\text{Se}_3$  and  $\text{AsSe}$  respectively). Se is quite a different story: only about 60% of the Se are twofold coordinated in both systems and there are nearly identical numbers of singly and triply coordinated Se (once again supporting the valence alternation pair picture, even in binary Se glasses [18]). Where chemical order is concerned,  $\text{As}_2\text{Se}_3$  has 77% As–Se bonds, 11% As–As bonds, and 12% Se–Se bonds. In  $\text{AsSe}$ , 68% of the bonds

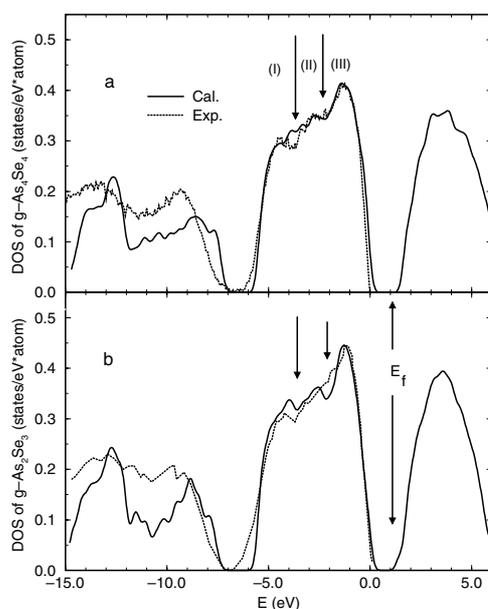


**Figure 3.** Pair correlations in As–Se glasses: (A) the radial distribution function  $G(r)$  for As–Se glasses; note the close similarity between the two compositions until  $r \approx 6$  Å; (B) the total static structure factor  $F(Q)$  from experiment (see [13]) and theory; the top panel is for  $\text{As}_2\text{Se}_3$  and the bottom panel for  $\text{AsSe}$ . The figure is reproduced from [13].



**Figure 4.** The VDOS of As–Se glasses, from [13].

are As–Se, 26% As–As, and 6% Se–Se. It is of course obvious that there are ‘error bars’ on these numbers (since they are derived from only two models), but they may be taken as representative of the topology of the materials.



**Figure 5.** Experiment and theory for the electronic density of states for  $g\text{-As}_2\text{Se}_3$  and  $\text{AsSe}$ . Spectra were aligned at the maximum peak of the valence band, and the theoretical peaks were broadened by the experimental resolution. I–III refer to the distinct types of bonding discussed in the text. From [16].

In figure 4, we present the VDOS for  $\text{As}_2\text{Se}_3$  and  $\text{AsSe}$ . For  $\text{As}_2\text{Se}_3$  the predicted DOS is in satisfactory agreement with inelastic neutron scattering measurements [13]. To our knowledge, experimental information about the VDOS is unavailable for  $\text{AsSe}$ , so the curve in figure 2 is actually a *prediction*. So as not to exaggerate our results, we note that both in theory and experiment, the VDOS is rather featureless except for the generic acoustic/optical structure that one would anticipate for any such material.

Photoemission is a standard experimental probe of the electronic density of states. In figure 5, we compare the experimental x-ray photoemission spectroscopy (XPS) results for the electronic valence band to our calculations [16]. The agreement is remarkably good in the valence band though, as always, the disorder ‘smears out’ the effects making both experiment and theory less structured (and therefore less informative) than one would like. The only ‘adjustable parameter’ in this calculation was the alignment of the spectra at the peak of the valence density of states. Elsewhere [16], we show that both  $g\text{-As}_2\text{Se}_3$  and  $a\text{-AsSe}$  may be understood as being constructed from primitive entities or ‘building blocks’. These building blocks are  $\text{AsSe}_3$  and  $\text{Se}_2\text{As-AsSe}_2$  as described above (for details see [14]). As a by-product of these simulations, we have Kohn–Sham states available, which may *loosely* be interpreted as approximate quasiparticle states [17]. By examining the structure of these states as a function of energy, we can readily infer the microscopic origin of the state (e.g. which atoms, or collection of atoms, give rise to a particular state). We find that the valence band may be thought of as consisting of three overlapping subbands (I–III) with the physical interpretation that I arises from intra-block bonding (in the sense of the ‘building blocks’ mentioned above), group II from inter-block bonding, and III is just the lone pair p band (at the valence edge) expected from the chemistry of the material. Thus, for the valence band at least, we find that it is appropriate to understand the states as being ‘inter-block’ (meaning that there is a block

analogue of bond charge built up between the blocks) or ‘intra-block’ (no bond charge between blocks, only within blocks).

#### 4. Conclusions

In this paper we have discussed general issues associated with the modelling of glasses. We provided a specific example for g-GeSe<sub>2</sub>, through which it was shown that a very different starting point (a relaxed tetrahedral WWW network decorated with Se on the bond centres) produced a model close to the best ‘cook and quench’ model, and with some positive features (such as a ‘proper’ asymptotic behaviour of the Ge–Se  $S(Q)$  for large  $Q$ , which is not seen in the ‘cook and quench’ model). We emphasize the value of including *a priori* information to make the initial conformations used as the starting point for modelling glasses: short MD simulation times are extremely remote from ergodicity, and this limitation means that it is often necessary to ‘build in’ information rather than relying on the supposedly ‘unbiased’ cook and quench scheme. We have produced a reasonably realistic pair of models of both g-As<sub>2</sub>Se<sub>3</sub> and a-AsSe and have reviewed our recent work on AsSe and As<sub>2</sub>Se<sub>3</sub> glasses. The coordinates of the atoms for the models discussed in this paper may be obtained from drabold@ohio.edu.

#### Acknowledgments

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