Quench-rate and size-dependent behaviour in glassy Ge$_2$Sb$_2$Te$_5$ models simulated with a machine-learned Gaussian approximation potential

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Abstract
Phase-change memory materials are promising candidates for beyond-silicon, next-generation non-volatile-memory and neuromorphic-computing devices; the canonical such material is the chalcogenide semiconductor alloy Ge$_2$Sb$_2$Te$_5$. Here, we describe the results of an analysis of glassy molecular-dynamics models of this material, as generated using a newly developed, linear-scaling (O(N)), machine-learned, Gaussian approximation potential. We investigate the behaviour of the glassy models as a function of different quench rates (varied by two orders of magnitude, down to 1 K ps$^{-1}$) and model sizes (varied by two orders of magnitude, up to 24 300 atoms). It is found that the lowest quench rate studied (1 K ps$^{-1}$) is comparable to the minimum cooling rate needed in order completely to vitrify the models on quenching from the melt.

Supplementary material for this article is available online

Keywords: phase-change memory, molecular-dynamics, quench rate, finite size, Ge–Sb–Te

(Some figures may appear in colour only in the online journal)

1. Introduction
Current electronic memory devices are based on silicon complementary metal-oxide-semiconductor (CMOS) technology, but the roadmap for Moore’s law continuing for such non-volatile (flash) memories, consisting of floating-gate (FG) MOS, field-effect transistor (FET) devices, is predicted to be nearing its end [1]. This is due to memory volatility occurring in such devices via electrons, trapped on the FG, tunnelling away through the very thin layers of dielectric, separating the FG and the semiconductor interface, associated with extreme down-scaling of device features. Thus, a new non-volatile memory (NVM) technology is required in order to bypass this technological-roadmap block, which is capable of further down-scaling. Phase-change random-access memory (PCRAM) is one such contender [2], and which is already being commercialized in the Micron-Intel Optane$^\text{TM}$ solid-state memory device, based on 3D-Xpoint$^\text{TM}$ cross-bar technology, and widely believed to use a PC material as the NVM element. PCRAM materials exhibit rather unique properties: they are electrically conducting in the crystalline (c-)state (logic state ‘1’) but electrically resistive in the glassy (g-)state (logic state ‘0’); they can be switched repeatedly and reversibly between metastable c- and g-states (the phase change), with the rate-limiting crystallization times being of the order of a few nanoseconds; and the PC behaviour scales down to ~2 nm.
The canonical PCRAM material is Ge$_2$Sb$_2$Te$_5$ (GST225), a composition along the pseudo-binary GeTe-Sb$_2$Te$_3$ tie-line of ternary Ge–Sb–Te semiconductor alloys. Although GST225 exhibits PC behaviour which is sufficient for PCRAM devices, the properties are sub-optimal in many regards [1]: the crystallization time is rather long (~10 ns); the electrical-resistance contrast between g- and c-phases is insufficient for significant multilevel programming, in which multiple metastable resistance levels (corresponding to different g-/c-volume proportions) can be written into the same memory cell, thereby permitting multi-bit per cell operation; resistance ‘drift’, a slow time-dependent increase in electrical resistance, is observed in the g-state, which is deleterious to multilevel operation. Thus, it is imperative to search for new PC compositions with improved behaviour, in order to develop next-generation PCRAM devices. But, in order to do so effectively, it is necessary first to understand thoroughly, at the atomistic level, the origin of the behaviour of GST225, so that any deficiencies in its performance can be understood and ameliorated in next-generation PC materials.

If expensive random-structure-searching efforts to find new PC materials are to be avoided, and a more rational material-design approach adopted, one needs to make use of the knowledge gained about the atomic origin of PC behaviour in canonical PCRAM materials by constructing realistic structural models of the technologically relevant phases. Such an approach can help to direct compositional and structural searches for new materials in order to ameliorate their property limitations and is particularly important for glassy materials which exhibit atomic disorder. The current state of the art, for generating (electronically) accurate models of glasses, is *ab initio* molecular dynamics (AIMD), as driven by density-functional theory (DFT) approximations. A number of such simulations of PC materials have been published, on the canonical GST225 composition [3–7] as well as on several others [8–10]. However, because such calculations are so computationally intensive (scaling cubically (O(N$^3$)) with the number of atoms, N, in the simulation box), this limits the maximum size of such models to ~500 atoms, the maximum simulation time to ~1 ns, and the number of simulations achievable in a given study to typically just one (thereby raising questions about the statistical significance of the calculated properties of such single, small models).

In order to circumvent these difficulties, it is necessary ideally to employ linear-scaling, O(N) interatomic potentials, which are able to approach DFT levels of energy and force accuracy. Such a potential was first constructed for the binary PC material, GeTe, by Sosso *et al* [11] using a neural-network, machine-learning method of fitting to the DFT-calculated electronic-potential-energy surfaces of representative atomic configurations. We were the first to develop an O(N) potential for the ternary Ge-Sb-Te system, in particular Ge$_2$Sb$_2$Te$_5$ [12], using a different machine-learning approach (Gaussian process regression [13], rather than a neural network). The resulting Gaussian approximation potential (GAP) is DFT-accurate, linear-scaling and reasonably chemically transferable (for other GST-based compositions) [12]. The O(N) capability of the GAP allowed for the simulation of an ensemble of 30 × 315-atom MD models of GST225 [14], with this model size dictated by the models being subsequently used for DFT calculations (with hybrid exchange-correlation functionals) of their electronic properties, specifically for a statistical examination of the occurrence of gap states.

In this paper, we turn to the other two distinct advantages of using (DFT-accurate) O(N) potentials, such as the GAP for GST225, viz. that long timescales can be accessed through simulations, and that sufficiently large models can be simulated in order to overcome finite-size effects. In particular, the ability to run longer molecular-dynamics trajectories translates into smaller values of the quench rate that can be used in vitrification simulations, as carried out from the equilibrated liquid; and the capability of simulating ultra-large models means that size effects on computed properties can be examined systematically.

### 2. Methods

Glassy GST225 structures were generated using classical MD simulations in cubic simulation cells with periodic boundary conditions. All the MD simulations were performed using the open-source LAMMPS (large-scale atomic/molecular massively parallel simulator) package [15].

The interactions between the atoms were modelled using a machine-learned ‘Gaussian approximation potential’ (GAP) [13], recently developed for the Ge-Sb-Te system by our group [12, 16]. This potential model exhibits an accuracy close to that of the underlying density-functional theory (DFT) training set of data, while its linear-scaling nature provides the opportunity to model very large structures and investigate slow cooling rates. The validity of the force field has been discussed in our previous work, demonstrating that the potential can be used for rigorous modelling of the short- and medium-range order structure of glassy GST225 [12]. In addition, the complex distribution of local environments that coexist inside the glass can be successfully reproduced; hence, glassy models generated with the GAP potential appear not to be missing any of the atomic environments present in glassy GST225 [14].

System-size effects were studied by generating four glassy structures, with a quench rate of 15 K ps$^{-1}$ and varying in size by nearly two orders of magnitude with respect to the total number of atoms in each periodic cell, namely, 315, 900, 7200 atoms and 24 300 atoms, while the cell size in each case was calculated from the experimental density (5.88 g cm$^{-3}$) [17], resulting in values of 21.65, 30.72, 61.44 and 92.27 Å, respectively (figure 1). In order to study the effect of the cooling rate, 900-atom glassy models were generated with six different quench rates, varying by two orders of magnitude, viz. 100, 50, 15, 10, 5 and 1 K ps$^{-1}$.

It is noted that, in this study, we have consistently quenched with a linear cooling rate from the melt in order to systematically study the structural changes upon cooling. However, glassy models can be generated also with step-wise quenches [18–24], in which case the choice of cooling schedule can further influence the glassy structure. Ultimately, one would expect the quench rate in real devices to decrease with
Figure 1. Melt-and-quench GAP models of glassy Ge$_2$Sb$_2$Te$_5$ of different sizes, quenched at a cooling rate of 15 K ps$^{-1}$ and shown roughly to scale; from left to right: 315, 900, 7200 and 24 300 atoms. Ge atoms (blue), Sb atoms (red) and Te atoms (yellow).

Figure 2. Configurational energy $U$ versus quench rate $\gamma$ for 900-atom models of amorphous Ge$_2$Sb$_2$Te$_5$ quenched at different rates (blue circles). The solid black line represents a logarithmic fit, with parameters: $U_0 = -4.027$ eV/atom, $a_1 = 6.025 \times 10^{-5}$, and $a_2 = 3.758$ (see equation (1)). The dashed line represents a power-law fit with parameters: $U_0 = -4.030$ eV/atom, $b_1 = 1.456 \times 10^{-3}$, and $b_2 = 0.742$ (see equation (2)) of the configurational energy $U$ as a function of the quench rate $\gamma$. The configurational energies of models of 315 (orange), 7200 (green), and 24 300 (red) atoms quenched at 15 K ps$^{-1}$ are shown for comparison.

3. Results
3.1. Configurational energy

The configurational energy ($U$) of glass models obtained from melt-and-quench MD simulations was shown to have a
The calculated average configurational energy of the different GST225 models was estimated from the production runs at room temperature carried out at the end of each melt-quench simulation. The resulting changes in configurational energy with quench rate for the GAP-generated amorphous GST225 models are given in figure 2. Two models are clear outliers, whether equation (1) or equation (2) was used for fitting the change in configurational energy with the cooling rate. These correspond to the cooling-rate extremes considered here. The model that was quenched with the smallest rate of 1 K ps$^{-1}$ has a much smaller configurational energy compared to the other amorphous models, and also smaller than the asymptotic limit for a glassy configuration, suggesting that it may be below the smallest critical quench rate needed for vitrification. When it comes to the model quenched at a relatively fast rate of 100 K ps$^{-1}$, it was found to show a very similar configurational energy to the one obtained from the 50 K ps$^{-1}$ model. Fast cooling rates of 100 K ps$^{-1}$ were found to deviate from the logarithmic dependence of the configurational energy in a previous study of multi-component oxide glasses [21]. This, together with a wide variability in the configurational energy of the fast quenched model, could explain the deviation.

When it comes to finite-size effects, models of 900 and 24 300 atoms quenched at 15 K ps$^{-1}$ had very similar configurational energies to each other, whereas models with 315 and 7200 atoms, quenched at the same rate, had a slightly higher energy. This reveals a significant variability in the model energy but no clear size effect.

3.2. Structure factor

The short-range order of the generated amorphous models was characterized by calculating the static structure factor for each glass. The total structure factors were calculated from the inverse Fourier transform of the radial distribution functions (RDFs) calculated for the models. The neutron-diffraction structure factors of glassy GST225 melt-and-quench GAP models of different sizes are shown in figure 3. The same maximum wavevector, $Q_{\text{max}} = 25$ Å$^{-1}$, and a smoothing factor of $\sigma = 0.125$ were used in the calculation of the structure factor from the RDFs of all models. We compare the simulated structure factors with an experimental measurement [31], which is displayed as the black solid curve in figures 3 and 4.

Figure 3 shows that GST225 GAP models are not significantly influenced by finite-size effects, at least beyond 900 atoms. A small difference can be seen in the low wavevector region of the smallest 315-atom model, when compared to the rest; nevertheless, the main features are largely the same.

Prompted by recent work on the system-size dependence of the fragile-to-strong transition in bulk metallic glasses [32, 33], we have carried out an Ornstein–Zernike analysis of the reduced pair-distribution function, $G(r)$, along the lines of [34], for the largest glassy GST225 model containing 24 300 atoms. Details of this analysis can be found in the supporting information. We find that the sizes of all models considered in this work exceed the longest correlation length (5.6 Å for Te-Te correlations) by a factor of more than three, in agreement with the observation that any finite-size effects are limited to the medium and extended-range order of the glass. It is worth noting that the first reports of crystallization of the glass consisted of models that already exceeded this correlation length, although not by a large enough margin to rule out finite-size effects [5].

By contrast, the structure factors of the 900-atom models, quenched at different rates, show a sharpening of all the peaks with decreasing cooling rate, especially below 5 K ps$^{-1}$ (figure 3). This sharpening of the peaks in the structure factor is an indication of structural ordering and possible partial crystallization for the slowest quench rate, while the appearance
of shoulders of the different peaks suggest potential phase segregation within the structure.

In order to visualize the resulting structure, the 900-atom glassy GST225 melt-and-quench GAP model quenched at 1 K ps$^{-1}$ is shown in figure 5. On visual inspection, the model seems to have segregated into GeTe- and SbTe-rich regions, and shows partial crystallization associated with the formation of ordered 4-membered square rings.

We note that a significant dependence of the low-$Q$ features of the structure factor of amorphous silica on the cooling rate has been reported in a previous simulation study [29], highlighting modifications in the medium-range structure of the glass when the cooling rate is decreased to values between 1–5 K ps$^{-1}$.

3.3. Chemical order

In order to capture chemical order in the amorphous structure, the binary order parameter of Cargill and Spaepen has been calculated [35], from the perspective of the quasi-binary (A/B) classification which is widely used in the phase-change materials community [36]. This classification groups Ge and Sb ions together as type ‘A’ and leaves Te as type ‘B’, highlighting the prevalent pattern of A-B alternation which is observed in most phase-change materials [37]. The quasi-binary chemical order parameter of a given structure is given by:

$$\eta_{AB}^0 = \frac{n_{AB} - 1}{n_{XX}}$$

(3)

where $n_A$ and $n_B$ are the atomic fractions of each (generic) atom type. The quantities $n_A$ and $n_B$ are the average coordination numbers of A and B atoms. The quantities $n_{AB}$ and $n_{BA}$ are the average number of B atoms around A, and the average number of A atoms around B, respectively. Finally, $n$ is the total average coordination number of the structure and the parameter $\eta_{AB}^{\text{max}}$ is given by:

$$\eta_{AB}^{\text{max}} = \begin{cases} x_B n_B, & x_B n_B \leq x_A n_A \\ x_A n_A, & x_A n_A > x_B n_B. \end{cases}$$

(4)

A related order parameter, denoted by $\alpha_x$ (where $x = \text{Ge, Sb, Te}$) can be obtained in order to highlight the difference in quasi-binary chemical order of an amorphous structure from the perspective of each species. This parameter has been used in a previous simulation study [4] to describe chemical order in GST225 and is given by:

$$\alpha_x = \begin{cases} 1 - \frac{n_{AB}}{x_A x_B (n_A + n_B)}, & x = \text{Ge, Sb} \\ 1 - \frac{n_{AB}}{x_A x_B (n_A + n_B)}, & x = \text{Te}. \end{cases}$$

(5)

The two approaches share a common interpretation, namely that a value of 1 signifies a fully ordered structure, such as the ideal cubic phase, a value of 0 signifies a random arrangement and finally, a value of $-1$ signifies a tendency for clustering, or phase separation. The amorphous GAP structures generated in this work have chemical order parameters between 0.7 and 0.95 in all cases, which are very close to those reported from DFT simulations of melt-quenched amorphous models of GST225 [2–7]. We note, though, that GAP glassy models are slightly overstructured, with an increased proportion of chemically ordered (AB) bonds and a lower fraction of tetrahedral Ge, when compared to similarly generated DFT models, as mentioned in our previous work [12].

Figure 5. Amorphous Ge$_2$Sb$_2$Te$_5$ melt-and-quench GAP model with 900 atoms, quenched at a rate of 1 K ps$^{-1}$. The formation of 4-fold square rings is visible and the structure seems to segregate into GeTe- and SbTe-rich regions respectively. The model nevertheless seems only partially crystalline, as significant disorder and some homopolar bonding remains.

Figure 6. Chemical-order parameters for melt-quenched glassy Ge$_2$Sb$_2$Te$_5$ GAP models, generated with a quench rate of 15 K ps$^{-1}$, versus the logarithm of the number of atoms in the simulation cell.
the amorphous models has no clear influence on the chemical order, as can be seen in figure 6. By contrast, slower cooling rates result in an increase of the chemical order, as seen in figure 7, with two regimes, below and above 5 K ps⁻¹ (or 5 × 10¹² K s⁻¹).

3.4. Bond and dihedral angles

Moving on to real-space structural indicators, the bond- and dihedral-angle distributions were calculated. Given the significant amount of chemical order present in all of the amorphous models, only the bond angles made from quasi-binary ordered triplets (Te–Ge–Te and Te–Sb–Te), and dihedral angles from quasi-binary ordered quartets (Te–Ge–Te–Ge and Te–Sb–Te–Sb), were analysed.

The distributions of Te–Ge–Te and Te–Sb–Te angles for models of different sizes, as well as for models generated with different cooling rates, are shown in figure 8. The usual distribution centred just below 90° corresponding to angles from defective octahedral environments, and a smaller peak in the region below 180° due to the angles formed between axial bonds, is observed in both cases [38]. The reason for the distortion away from the ideal octahedral angles of 90° and 180° is the presence of lone-pair electrons which occupy a larger volume than bonded electrons, as predicted by VSEPR theory [39]. The lone pairs ‘push’ the bonded atoms closer together and reduce these bond angles. The effect is larger for Sb-centred angles, due to the larger Sb-centred angles due to the large volume occupied by Sb lone pairs when compared to Ge lone pairs.

A small number of tetrahedral Ge environments have been identified in all of the models, corresponding to the density of angles around 109.5°. As previously reported, the fraction of tetrahedra in the GAP glassy models (6%–11%) is lower when compared to DFT studies, leading to overstructured models [12].

Overall, the angular distributions become slightly wider in models with a larger size, and narrower, and hence more ordered, as the cooling rate is reduced. The Te–Ge–Te bond-angle distribution becomes more ordered in response to the slower quench rate, when compared to the behaviour of the Te–Sb–Te bond-angle distribution, which remains relatively unchanged.

Compared to the bond-angle distribution functions, the dihedral angular distribution functions are more sensitive to both the finite-size effects and the cooling rate. They nevertheless tell a similar story, as topological ordering is observed from an increase in the peaks around φ = 90° and 180°, and a decrease of the intensity around φ = 45° and 135°, is observed in smaller models, in figures 9(a) and (b). Models obtained with a slower cooling rate also become more ordered, as shown in figures 9(c) and (d), and torsions about Ge–Te bonds respond more strongly to the ordering effects compared to those around Sb–Te bonds.

The tetrahedral angular order parameter of Errington and Deh Benedetti [40], for an atom i, is given by:

\[ q_4 = 1 - \frac{3}{8} \sum_{j=1}^{n} \sum_{k=j+1}^{n} \left( \cos (\theta_{jk}) + \frac{1}{3} \right)^2 \]  

where the j and k indices run over nearest neighbours of atom i. This parameter is 0 for an ideal gas or an octahedral environment and 1 for a tetrahedral local environment. Other important values are \( \frac{1}{6} \) for a 3-coordinated pyramidal environment, \( \frac{1}{8} \) for a 4-fold coordinated defective octahedron (see-saw structure) and \( \frac{1}{5} \) for a 5-fold defective octahedron (square pyramidal environment). Figure 10 shows the change in the distribution of the \( q_4 \) parameter with the quench rate. From 100 K ps⁻¹ to 10 K ps⁻¹, the distribution moves towards more pyramidal and tetrahedral environments. Below 10 K ps⁻¹, however, the structure starts to become more octahedral with a dramatic change below 5 K ps⁻¹. For the 1 K ps⁻¹ model, we obtain a wide distribution corresponding largely to octahedral and defective octahedral environments.

3.5. Rings

Shortest-path ring statistics were calculated using the Franzblau algorithm [41] as implemented in the QUIP code [42]. The resulting ring distributions are shown for models of different sizes in figure 11, while those of models quenched at different rates can be seen in figure 12. The 4-fold ring is the most probable one in all cases, and this is expected since it is an important structural motif in phase-change memory materials. ABAB square rings are also building blocks of the cubic crystalline phase and play an important role during the fast crystallization of the amorphous phase [4, 37].

Models of a smaller size, as well as those that have been quenched more slowly, show an increased amount of topological order. The 315-atom model has a slightly higher proportion of 4-fold shortest-path rings compared to larger models. Cooling rates have a more significant effect, especially below 5 K ps⁻¹, when the proportion of 4-, 6- and 8-fold shortest-path rings increases sharply, indicating structural ordering and, in particular, possible partial crystallization.
Figure 8. Bond-angle distribution functions of: (a) Te–Ge–Te angles and (b) Te–Sb–Te angles in models of amorphous Ge$_2$Sb$_2$Te$_5$ of different sizes (from yellow to red in increasing order); (c) Te–Ge–Te and (d) Te–Sb–Te angles in models of amorphous Ge$_2$Sb$_2$Te$_5$ quenched at different rates (darker shades of green as the cooling rate decreases).

Figure 9. Dihedral-angle distribution functions of: (a) Te–Ge–Te–Ge and (b) Te–Sb–Te–Sb dihedral angles in models of amorphous Ge$_2$Sb$_2$Te$_5$ of different sizes (from yellow to red in increasing order); (c) Te–Ge–Te–Ge and (d) Te–Sb–Te–Sb dihedral angles in models of amorphous Ge$_2$Sb$_2$Te$_5$ quenched at different rates (darker shades of green as the cooling rate decreases).

3.6. Voids

The GST225 material has intrinsic vacancies and exhibits cation disorder even as a cubic crystal. Metallic or degenerate semiconductor compositions that are fully-filled ‘rocksalt-like’ structures (such as GST224 or even GeTe) can lower their energy by forming cation vacancies, as well as by undergoing structural distortions, with the GST225 composition being close to the energetically optimal amount of cation vacancies [43]. The distribution of these vacancies within the crystalline lattice has been shown to be correlated with properties of the material, and to govern metal-insulator and
Figure 10. Tetrahedral angular order parameter $q_4$ for 900-atom glassy GST225 models quenched at different rates. Darker shades of green correspond to slower cooling rates from 100 K ps$^{-1}$ to 1 K ps$^{-1}$.

Figure 11. Shortest-path ring statistics in models of amorphous Ge$_2$Sb$_2$Te$_5$ of different sizes (from yellow to red in increasing order of model size from 315 to 24 300 atoms). Error bars reflect the variation over multiple configurations sampled at 300 K.

Figure 12. Shortest-path ring statistics in amorphous models of Ge$_2$Sb$_2$Te$_5$ obtained using different cooling rates; darker shades of green as the cooling rate decreases from 100 K ps$^{-1}$ to 1 K ps$^{-1}$.

Furthermore, different amorphous phases have also been identified as a function of pressure [46].

In order to further describe the changes in the topology of the glassy network, the statistics of non-interstitial voids within the structure were evaluated for the different glassy GST225 models. These voids have been identified on a fine mesh, with a maximal spacing of 0.3 Å, using a Voronoi construction with a cutoff of 2.8 Å [45]. The probability density of voids in the amorphous structure, assumed to be spherical with a radius $r$, was fitted using a log-normal distribution, as prompted by previous studies on vitreous silica [47, 48].

The resulting probability distributions of voids, as a function of the radius, for amorphous GST225 models of different sizes are shown in figure 13. The distribution of voids becomes sharper with increasing number of atoms, while the total void volume remains roughly the same. Therefore, it is more likely to find smaller voids in larger models.

The void distribution as a function of the quench rate is shown in figure 14. For quench rates higher than 5 K ps$^{-1}$, there is a gradual sharpening of the distribution as the quench rate is lowered from 100 K ps$^{-1}$ down to about 10 K ps$^{-1}$. The distribution of voids for a quench rate of 5 K ps$^{-1}$ is broader than for 10 K ps$^{-1}$ but still sharper than for 50 or 100 K ps$^{-1}$. The void distribution changes dramatically below a quench rate of 5 K ps$^{-1}$. Given the significant density difference between the amorphous and crystalline phases of GST225, the much wider void-size distribution obtained for a quench rate of 1 K ps$^{-1}$ is another indicator of partial crystallization in this case. The cubic crystalline phase of GST225 is known to have a significant number of "cation" vacancies, but it nevertheless has a higher density (6.30 g cm$^{-3}$) than the corresponding amorphous phase (5.88 g cm$^{-3}$). Given that the volume of the cells was kept constant during the quench, to maintain the experimental amorphous density, it is not surprising that large voids appear when the system is cooled slowly enough, as it tries to form a denser crystalline phase, instead of the glass.

cubic-to-hexagonal transitions in GST225 [44]. While vacancies cannot be clearly defined in the absence of a crystalline lattice, voids play a similar role in the glassy GST225 material where they were shown to enhance ionic diffusion [45].
shown as vertical lines above the meter might be low due to the formation of large voids in the largest models. The order parameter for crystallization, the number of ABAB square rings, is nearly 70% that of an ideal cubic crystal. Considering the low configurational energy, the increased proportion of ABAB square rings, and the local densification of the structure, we believe the 1 K ps\(^{-1}\) model to be partially crystalline.

4. Discussion

The above-mentioned results from a study of model-size and quench-rate effects on the structure of glassy models of GST225, simulated using the linear-scaling GAP potential, generally match expectations. For instance, it is understandable that the contribution of larger rings to the ring-size distribution should be diminished in smaller-size models (especially in the smallest 315-atom model), and revealed in the largest models (figure 11). The ring-size distributions for all the simulated glassy models show a clear even-odd alternation, indicative of the medium-range order present in these glassy structures and resulting from the prevalence of 4-membered (ABAB-like) rings, a structural memory of the metastable rocksalt crystal structure of this material. Equally, the secondary maximum in the distribution for 12-rings, evident in figure 11, is significantly reduced with increasing model size and illustrates the changes in the medium-range order of the material.

However, there are many more pronounced quenching-rate effects, especially for the slowest quench rates. For instance, the numbers of 4- and 6-rings, and to a lesser extent of 8-rings, are greatly enhanced for the slowest quench rate, 1 K ps\(^{-1}\) (figure 12). The dihedral-angle distribution also sharpens appreciably for the slowest quench rate, particularly for Te–Ge–Te–Ge dihedral angles (figure 9(c)). The Ge-centred (not the Sb-centred, interestingly) bond-angle distribution shows a similar effect for near-90° bond angles (figure 8). Furthermore, the total structure factor exhibits fine structure, reminiscent of the presence of crystallinity, for the slowest quench rate GST225 model (figure 4). The second largest component of the Fourier transform (FFT) of the atomic density in the case of the 1 K ps\(^{-1}\) model, commonly used as an order parameter for crystallization [5, 12], is low (0.25) when compared to crystalline models at a higher density (>0.8), but is more than double that of the other glassy models at the experimental amorphous density (~0.11). Being sensitive to the periodicity of the structure, the FFT order parameter might be low due to the formation of large voids in this model. The number of ABAB square rings, also used as an order parameter for the crystallization [12, 37], is nearly 70% that of an ideal cubic crystal. Considering the low configurational energy, the increased proportion of ABAB square rings, and the local densification of the structure, we believe the 1 K ps\(^{-1}\) model to be partially crystalline.

The pattern in the chemical order and tetrahedral angular order parameter \(q_4\) corroborate three distinct regimes in quenched GST225. For very fast quenches, faster than 100 K ps\(^{-1}\), the structure resembles that of the frozen liquid. Below this value, we see significant AB-ordering and the \(q_4\) parameter indicates the formation of pyramidal and tetrahedral environments. The familiar structure of glassy GST225, similar to that previously reported from DFT computational studies, is obtained around 10 K ps\(^{-1}\). This ordering process, together with the formation of tetrahedral environments, is in agreement with the idea that an ‘ideal’ amorphous phase can be distinguished from both the liquid and the crystalline phases due to the formation of tetrahedral local environments. Finally, below 5 K ps\(^{-1}\), the structure undergoes another dramatic ordering process and becomes more connected and almost entirely octahedral, resembling the metastable cubic crystal structure instead of the glass.

Thus, from these quench-rate-dependent simulation results, it can be concluded that, for this (GAP) interatomic potential for GST at least, the critical quench rate, below which liquid GST225 cannot be vitrified, lies in the range 1–5 K ps\(^{-1}\) (1–5 × 10\(^{12}\) K s\(^{-1}\)), and probably nearer the lower value than the upper one. This estimate is in very good agreement with recent DFT-based MD simulations of GST225, using the PBE exchange-correlation functional, where the critical quench rate was estimated to be 4.5 K ps\(^{-1}\) [49]. However, it should be noted that these DFT-based simulations were for rather small model sizes (109 atoms, rather than the 900-atom models used in the corresponding present GAP-MD simulations), and so their estimate for the critical vitrification quench rate might be somewhat too high, since it is generally easier to crystallize small models than larger models (of a similar density), due to finite-size effects.

![Figure 14. Void statistics in amorphous models of Ge\(_2\)Sb\(_2\)Te\(_5\) obtained using different cooling rates; darker shades of green as the cooling rate decreases from 100 K ps\(^{-1}\) to 1 K ps\(^{-1}\). Solid lines are log-normal fits to the data. Each of the void radii obtained from the analysis are shown as vertical lines above the x-axis.](image-url)
5. Conclusions

We report the results of a series of molecular-dynamics simulations of the canonical phase-change non-volatile memory material, GST225, made using a new, linear-scaling, machine-learned interatomic (GAP) potential. We have explored the effects of model size, varying the number of atoms in the simulation cells by nearly two orders of magnitude (up to 24 300 atoms), and of quench rate, again varied by two orders of magnitude, down to 1 K ps$^{-1}$ ($10^{12}$ K s$^{-1}$). It was found that, for the slowest quench rate, the models were partially crystalline rather than glassy, and so this value of quench rate gives an estimate for the critical minimum quench rate from the liquid, below which this phase-change material cannot be vitrified.

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References

[1] Theis T N and Wong H-S P 2017 The end of Moore’s law: a new beginning for information technology computing Sci. Engineer. 19 41
[2] Noé P, Vallée C, Hippert F, Fillot F and Raty J Y 2018 Phase-change materials for non-volatile memory devices: from technological challenges to materials science issues Semicond. Sci. Technol. 33 013002
[3] Caravati S, Bernasconi M, Kühne T D, Krack M and Parrinello M 2009 Coexistence of tetrahedral- and octahedral-like sites in amorphous phase change materials Appl. Phys. Lett. 91 171906
[4] Akola J and Jones R O 2007 Structural phase transitions on the nanoscale: the crucial pattern in the phase-change materials Ge$_2$Sb$_2$Te$_5$ and GeTe Phys. Rev. B 76 235201
[5] Hegedüs J and Elliott S R 2008 Microscopic origin of the fast crystallization ability of Ge–Sb–Te phase-change memory materials Nat. Mater. 7 399
[6] Akola J and Jones R O 2008 Density functional study of amorphous, liquid and crystalline Ge$_2$Sb$_2$Te$_5$: homopolar bonds and/or AB alternation? J. Phys.: Condens. Matter 20 465103
[7] Caravati S, Bernasconi M, Kühne T D, Krack M and Parrinello M 2009 First-principles study of crystalline and amorphous Ge$_2$Sb$_2$Te$_5$ and the effects of stoichiometric defects J. Phys.: Condens. Matter 21 255501
[8] Caravati S, Bernasconi M and Parrinello M 2010 First-principles study of liquid and amorphous Sb$_2$Te$_3$ Phys. Rev. B 81 014201
[9] Kalikka J, Akola J, Jones R O, Kohara S and Usuki T 2012 Amorphous Ge$_2$Te$_5$: density functional, high-energy x-ray and neutron diffraction study J. Phys.: Condens. Matter 24 015802
[10] Ropo M, Akola J and Jones R O 2017 Crystalization of supercooled liquid antimony: a density functional study Phys. Rev. B 96 184102
[11] Sosso G C, Miceli G, Caravati S, Behler J and Bernasconi M 2012 Neural network interatomic potential for the phase change material GeTe Phys. Rev. B 85 174103
[12] Mocanu F C, Konstantinou K, Lee T H, Bernstein N, Deringer V L, Csányi G and Elliott S R 2018 Modeling the phase-change memory material, Ge$_2$Sb$_2$Te$_5$, with a machine-learned interatomic potential J. Phys. Chem. B 122 8998
[13] Bartók A P, Payne M C, Kondor R and Csányi G 2010 Gaussian approximation potentials: the accuracy of quantum mechanics, without the electrons Phys. Rev. Lett. 104 136403
[14] Konstantinou K, Mocanu F C, Lee T H and Elliott S R 2019 Revealing the intrinsic nature of the mid-gap defects in amorphous Ge$_2$Sb$_2$Te$_5$ Nat. Commun. 10 3065
[15] Plimpton S 1995 Fast parallel algorithms for short-range molecular dynamics J. Comput. Phys. 117 1–19
[16] Mocanu F C 2018 First and second-principles atomistic modelling of Ge–Sb–Te phase-change memory materials PhD Dissertation Cambridge University
[17] Njoroge W K, Wöltgens H W and Wittig M 2002 Density changes upon crystallization of Ge$_2$Sb$_2$Te$_5$ thin films J. Vac. Sci. Technol. A 20 230
[18] Cormack A N and Du J 2001 Molecular dynamics simulations of soda-lime-silicate glasses J. Non-Cryst. Solids 293–295 283
[19] Pedone A, Malavasi G, Menziani M C, Cormack A N and Serge U 2006 A new self-consistent empirical interatomic potential model for oxides, silicates, and silica-based glasses J. Phys. Chem. B 110 11780
[20] Du J and Xiang Y 2012 Effect of strontium substitution on the structure, ionic diffusion and dynamics properties of 4S5 Bioactive glasses J. Non-Cryst. Solids 358 1059
[21] Tiloca A 2013 Cooling rate and size effects on the medium-range structure of multicomponent oxide glasses simulated by molecular dynamics J. Chem. Phys. 139 114501
[22] Konstantinou K, Sushko P V and Duffy D M 2015 Structure and ionic diffusion of alkaline-earth ions in mixed cation glasses A$_x$O–2MO–4SiO$_2$ with molecular dynamics simulations J. Non-Cryst. Solids 422 57
[23] Pedesseau L, Ispas S and Kob W 2015 First-principles study of a sodium borosilicate glass-former. II. The glass state Phys. Rev. B 91 134202
[24] Konstantinou K, Sushko P V and Duffy D M 2016 Modelling the local atomic structure of molybdenum in nuclear waste glasses with ab initio molecular dynamics simulations Phys. Chem. Chem. Phys. 18 26125
[25] Tenenbaum A, Ciccotti G and Gallicco R 1982 Stationary nonequilibrium states by molecular dynamics. Fourier’s law Phys. Rev. A 25 2778
[26] Kantorovich L and Rompotis N 2008 Generalized Langevin equation for solids. II. Stochastic boundary conditions for nonequilibrium molecular dynamics simulations Phys. Rev. B 78 094305
[27] Konstantinou K, Lee T H, Mocanu F C and Elliott S R 2018 Origin of radiation tolerance in amorphous Ge2Sb2Te5 phase-change random-access memory material Proc. Natl Acad. Sci. 115 5353
[28] Konstantinou K, Mocanu F C, Lee T H and Elliott S R 2018 Ab initio computer simulations of non-equilibrium radiation-induced cascades in amorphous Ge2Sb2Te5 J. Phys.: Condens. Matter 30 455401
[29] Vollmayr K, Kob W and Binder K 1996 Cooling-rate effects in amorphous silica: a computer-simulation study Phys. Rev. B 54 15808
[30] Vollmayr K, Kob W and Binder K 1996 How do the properties of a glass depend on the cooling rate? A computer simulation study of a Lennard–Jones system J. Chem. Phys. 105 4714
[31] Jóvári P, Kaban I, Steiner J, Beuneu B, Schöps A and Webb M A 2008 Local order in amorphous Ge2Sb2Te5 and Ge1Sb2Te5 Phys. Rev. B 77 035202
[32] Sukhomlinov S V and Müser M H 2019 Anomalous system-size dependence of properties at the fragile-to-strong transition in a bulk-metallic-glass forming melt Comput. Mater. Sci. 156 129
[33] Alvarez-Donado R, Cajahuaranga S and Antonelli A 2019 Revisiting the fragile-to-strong crossover in metallic glass-forming liquids: application to Cu,Zr,Al100-x alloy Phys. Rev. Mater. 3 085601
[34] Sukhomlinov S V and Müser M H 2018 Quasidiscontinuous change of the density correlation length at the fragile-to-strong transition in a bulk-metallic-glass forming melt Phys. Rev. Mater. 2 115604
[35] Cargill G S and Spaepen F 1981 Description of chemical ordering in amorphous alloys J. Non-Cryst. Solids 43 91
[36] Akola J, Larrueza J and Jones R O 2011 Polymorphism in phase change materials: melt-quenched and as-deposited amorphous structures in Ge2Sb2Te5 from density functional calculations Phys. Rev. B 83 094113
[37] Kalikka J, Akola J and Jones R O 2016 Crystallization processes in the phase change material Ge2Sb2Te5: unbiased density functional/molecular dynamics simulations Phys. Rev. B 94 134105
[38] Lee T H and Elliott S R 2017 The relation between chemical bonding and ultrafast crystal growth Adv. Mater. 29 1700814
[39] Gillespie R 2000 Improving our understanding of molecular geometry and the VSEPR model and the analysis of electron density distributions Coord. Chem. Rev. 197 51
[40] Errington J R and Debenedetti P G 2001 Relationship between structural order and the anomalies of liquid water Nature 409 318
[41] Franzblau D S 1991 Computation of ring statistics for network models of solids Phys. Rev. B 44 4925
[42] Bartók A P and Csányi G 2015 Gaussian approximation potentials: a brief tutorial introduction Int. J. Quant. Chem. 115 1051
[43] Wuttig M, Lüsebrink D, Wamwangi D, Welnic W, Gilleßen M and Drönkowski R 2007 The role of vacancies and local distortions in the design of new phase-change materials Nat. Mater. 6 122
[44] Zhang W, Thiess A, Zalden P, Zeller R, Dederichs P H, Raty J-Y, Wuttig M, Blügel S and MazzaRello R 2012 Role of vacancies in metal–insulator transitions of crystalline phase-change materials Nat. Mater. 11 952
[45] Lee T H and Elliott S R 2011 Structural role of vacancies in the phase transition of Ge2Sb2Te5 Phys. Rev. B 84 094124
[46] Sun Z, Zhou J, Pan Y, Song Z, Mao H-K and Ahuja R 2011 Pressure-induced reversible amorphization and an amorphous–amorphous transition in Ge2Sb2Te5 phase-change memory material Proc. Natl Acad. Sci. 108 10410
[47] Shackelford J F and Masaryk J S 1978 The interstitial structure of vitreous silica J Non-Cryst. Solids 30 127
[48] Chan S L and Elliott S R 1991 Theoretical study of the interstice statistics of the oxygen sublattice in vitreous SiO2 Phys. Rev. B 44 442
[49] Brancio P S, Bai K, Ramanarayan H, Wu D T, Sullivan M B and Srolovitz D J 2018 Atomistic insights into the nanosecond long amorphization and crystallization cycle of nanoscale Ge2Sb2Te5: an ab initio molecular dynamics study Phys. Rev. Mater. 2 043401