Note: Accounting for pressure effects on the calculated equilibrium structure of glassy GeSe$_2$

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Unambiguous neutron diffraction data have shown that the structure of glassy GeSe₂ (x = 0.33 composition within the Ge$_x$Se$_{1-x}$ family) consists of a variety of structural units, encompassing GeSe₄ tetrahedra, homopolar bonds, and defective Ge–Se coordinations, accounting for a moderate departure from chemical order.[1–3] This picture has been substantiated by first-principles molecular dynamics (FPMD) results obtained within the density functional theory (DFT) framework.[4,5,7] In spite of these successes, it remains to be understood why the number of Ge atoms involved in edge-sharing and corner-sharing connections or the number of Se atoms involved in homopolar bonds differ markedly from the experimental results (see Table I). Analysis of the methodology employed within FPMD reveals that most simulations (intended to be stress-free at equilibrium) have been performed at a fixed density. Indeed, no information on the actual values of the pressure is available.[5,7] Account of the pressure is worthwhile since the density vs pressure relationship holding experimentally might not be *exactly* reproduced by the DFT model.[6] As a consequence, undesirable pressure effects altering the room temperature equilibrium properties can be observed. This shortcoming exists regardless of the glass preparation method (quench from the liquid or, much less employed, solid state amorphization).

In this Note, we address this issue via a twofold approach. First, the volume of the periodic system is calibrated at T = 0 K by minimizing the non-negligible pressure (1/3 of the sum of the calculated stress tensor components) acting on the simulated periodic cell of Ref. 7. Then, we performed an extended FPMD simulation at room temperature, thereby allowing the system to adjust its structure to the new pressure conditions. Glassy GeSe₂ thereby obtained is more chemically ordered by featuring the correct proportions of Ge–Ge homopolar bonds, edge-sharing and corner-sharing connections.

In our theoretical framework, the electronic structure is described within density functional theory and evolves self-consistently during the motion.[8] Additional details on our methodology are extensively provided in a previous work.[5] Calculations on glassy GeSe₂ have been carried out in the past at T = 300 K for a number density $\rho^{\mathbf{a}}$ = 0.034 Å^{-3} (side length 15.16 Å), slightly larger than the value quoted in the experimental work ($\rho^{\mathbf{exp}}$ = 0.0334 Å^{-3}).[9,10] The value of the pressure associated with $\rho^{\mathbf{a}}$ was found to be definitely non-negligible (1 GPa). By expanding the side length

to 15.44 Å (density $\rho^{\mathbf{b}}$ = 0.0326 Å^{-3}) and further relaxing the whole structure, we were able to lower the pressure to less than ~0.1 GPa. The final relaxed configuration was selected to begin a thermal annealing cycle, featuring 40 ps at T = 300 K, 50 ps at T = 600 K, 150 ps at T = 900 K (to allow significant diffusion) and, on cooling, 70 ps at T = 600 K and 150 ps at T = 300 K, with statistical averages taken over a final portion of the trajectory lasting 20 ps at T = 300 K. We also performed an additional run (lasting 10 ps) by employing the constant pressure *NPT* Andersen technique[11] with zero pressure as target average value. Standard deviations and instantaneous values for the stress tensor diagonal and non-diagonal terms are not larger than 0.005 GPa and 0.12 GPa, respectively, this latter upper bound being much smaller than those calculated for $\rho^{\mathbf{a}}$ = 0.034 Å^{-3}. The average density for this *NPT* calculation is 0.0322 Å^{-3}, very close to $\rho^{\mathbf{b}}$ = 0.0326 Å^{-3}. Structural properties obtained within the *NVT* and the *NPT* trajectory do not differ significantly within statistical errors, estimated from the analysis carried out on Ref. 5 on glassy GeSe₂ where as many as six independent trajectories were produced.[12]

In Fig. 1, we display the calculated set of $g_{\alpha\beta}^{\mathbf{a}}(r)$,[7] $g_{\alpha\beta}^{\mathbf{b}}(r)$ (present results) and experimental $g_{\alpha\beta}^{\exp}(r)$ (Ref. 1) partial pair correlation function, α, β being Ge and/or Se. Integrals on the first coordination shell (coordination numbers $n_{\alpha\beta}$) are also provided. When comparing $g_{\alpha\beta}^{\mathbf{a}}(r)$ and $g_{\alpha\beta}^{\mathbf{b}}(r)$, small shifts in the peak positions are found within statistical fluctuations (typically of the order of 0.03-0.05 Å, Ref. 5). On the contrary, the $\rho^{\mathbf{b}}$ data mark a statistically significant improvement for $n_{\alpha\beta}$ (Fig. 1, insets), these properties reflecting both the intensity and the width of the peaks. Focussing on $g_{\mathrm{GeGe}}(r)$, the three main peaks in the region $2 \lesssim r(\text{Å}) \lesssim 4$ have been identified as arising, for increasing r, from homopolar Ge–Ge bonds, Ge atoms involved in edge-sharing connections, and Ge atoms involved in corner sharing connections, respectively. The new data improve upon those of Ref. 7 and reproduce the experimental trend of the three main peaks intensities in the region $2 \lesssim r(\text{Å}) \lesssim 4$, the second peak being less intense than the first one. As shown in Table I, we obtain an unprecedented agreement for the percentages of Ge and Se atoms involved in Ge–Ge and Se–Se homopolar bonds and for the percentages of Ge atoms found in edge-sharing and corner-sharing connections. This statement accounts for the statistical uncertainties (± 5 at most in percentage units) that can be attributed to the above quantities (see Ref. 5). Most
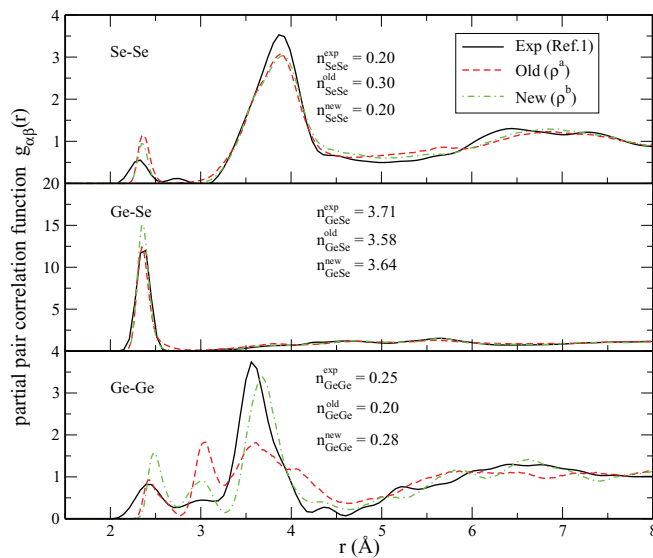
FIG. 1. Partial pair correlation functions for glassy GeSe$_2$. The experimental results of Ref. 1 (solid curve) are compared with the results of Ref. 7 (dashed red curve) and with the present results (*NVT* ensemble, dashed-dotted green curve).

FIG. 2. The Bhatia-Thornton concentration-concentration partial structure factor $S_{CC}(k)$ for glassy GeSe$_2$. (Solid line) Experimental results of Ref. 1. (Green curve) Present results (*NVT* ensemble). (Red curve) Results of Ref. 7.

remarkable is the improvement in the number of corner-sharing connections, stemming from the substantial change in the intensity and shape of the third main peak, in much better agreement with experiments than in the ρ^a case.

Releasing the residual pressure inherent in the previous results for ρ^a has the effect of enhancing the chemical order, with as many as 92% of Ge atoms being fourfold coordinated, 72% of them within a GeSe$_4$ tetrahedron. In Ref. 7, these values were equal to 78.1% and 62.5%, respectively.

Turning to the reciprocal space properties, a correct reproduction of the Bhatia-Thornton[13] concentration-concentration partial structure factor $S_{CC}(k)$ proved to be a stringent test for FPMD approaches.[14] Observation of Fig. 2 reveals that the intensity of the main peak of $S_{CC}(k)$, located at $k \sim 2$ Å^{-1} is very close to the experimental one for ρ^b. This same height was underestimated when working at the ρ^a density (Fig. 2). Also, a minimum is now visible in the range 4 Å$^{-1} < k < 5.5$ Å^{-1}. A detailed analysis (extended to sev-

eral independent trajectories) of pressure effects on the partial structure factors of glassy GeSe$_2$ studied within the *NVT* and *NPT* ensembles will be made available elsewhere.

In conclusion, account of residual pressure effects on the room temperature, equilibrium structure of glassy GeSe$_2$ leads to a better agreement between atomic-scale models and experiments for this prototypical network-forming disordered material.

TABLE I. N_{Ge-Ge} (N_{Se-Se}) is the percentage of Ge (Se) atoms in Ge–Ge (Se–Se) homopolar bonds, N_{Ge}(ES) is the percentage of Ge atoms forming edge-sharing connections and N_{Ge}(CS) is the percentage of Ge atoms forming corner-sharing connections. Note that in Ref. 4, a molecular dynamics approach was used in conjunction with a reverse Monte Carlo method.

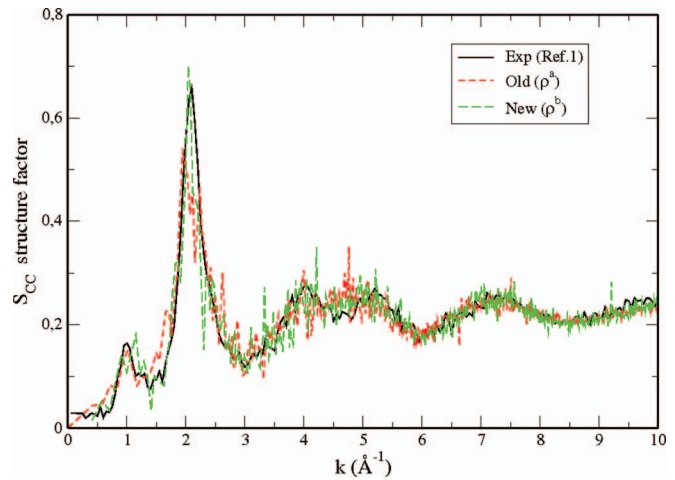|	$N_{Ge–Ge}$	$N_{Se–Se}$	N_{Ge} (ES)	N_{Ge} (CS)
Ref. 7	20	30	58	22
Ref. 4	17	30	38	45
This work	23	18	35	42
Experiment: Ref. 1	25	20	34	41

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