



Strain-induced deformation of the porous structure in binary glasses under tensile loading

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ABSTRACT

The evolution of porous structure and mechanical properties of binary glasses under tensile loading were examined using molecular dynamics simulations. We consider vitreous systems obtained in the process of phase separation taking place after a rapid isochoric quench of a glass-forming liquid to temperatures below the glass transition point. The porous structure in undeformed samples varies from a connected porous network to a random distribution of isolated pores with increasing average density. We find that the elastic modulus follows a power-law dependence on the average glass density and the shape of pore size distribution at small strain remains nearly the same as in quiescent samples. Upon further loading, the pores become significantly deformed and coalesce into larger voids that leads to formation of system-spanning empty regions associated with failure of the material.

1. Introduction

Recent progress in the development of porous structural materials with applications ranging from biomedicine to energy conversion and storage as well as civil infrastructure, requires a thorough understanding of their microstructure-property relationships [1,5,3,4,2]. An accurate pore characterization in microporous materials, which involves numerical analysis of the probe-accessible and -occupiable pore volume, allows determination of their permeability to guest molecules as well as internal void volume and surface area [6]. The results of experimental and computational studies have shown that mechanical properties of bulk metallic glasses with periodic arrays of pores are governed by shear localization between adjacent pores in a regime of plastic deformation [7–9]. Similar to ductile metallic alloys, it was found that in highly strained nanoporous silica glasses, multiple cracks are initiated at void surfaces, which leads to void coalescence and intervoid ligament failure [10]. It was further shown that mechanical properties of porous silica glasses are improved in samples with channel pore morphology rather than isolated pore configurations [11]. Despite extensive efforts, the precise connection between individual pore morphologies and elastic, shear and bulk moduli has not yet been determined.

During the last decade, the mechanical properties of metallic glass nanowires subjected to uniaxial tension have been extensively

investigated using molecular dynamics simulations [12–16] and experimental measurements [17–20]. It was found that, when the size of metallic glass samples is reduced down to the nanoscale, the deformation mode changes from brittle to ductile [15–20]. The difference in the deformation behavior can be visually detected by direct observation of either shear localization along a plane, called a shear band, or the formation of extended necking along the loading direction [12,18]. A subsequent analysis of irradiated samples that were emulated in MD simulations by randomly removing a small fraction of atoms, has shown an enhanced tensile ductility; while this effect is reduced if only the outer shell of a nanowire is rejuvenated [15]. In Ref. [14], it was shown that the brittle-to-ductile transition dependence on sample size, observed in nanoscale metallic glasses, is defined by a fundamental characteristic size effect in the failure mode under tensile loading. Specifically, it was argued that nanosized specimens with surface imperfections exhibit a clear transition from shear banding to necking instability, when the ratio of average surface imperfection size to sample diameter exceeds some characteristic value [14]. Furthermore, it was also demonstrated that a homogeneous bulk metallic glass under uniaxial tension exhibits only one dominant shear band, whereas multiple shear bands are initiated at interfaces between grains in a nanoglass [21]. Moreover, it was found that the shear-band orientation with respect to the loading direction is different in the cases of uniaxial compression and extension of two-dimensional athermal amorphous

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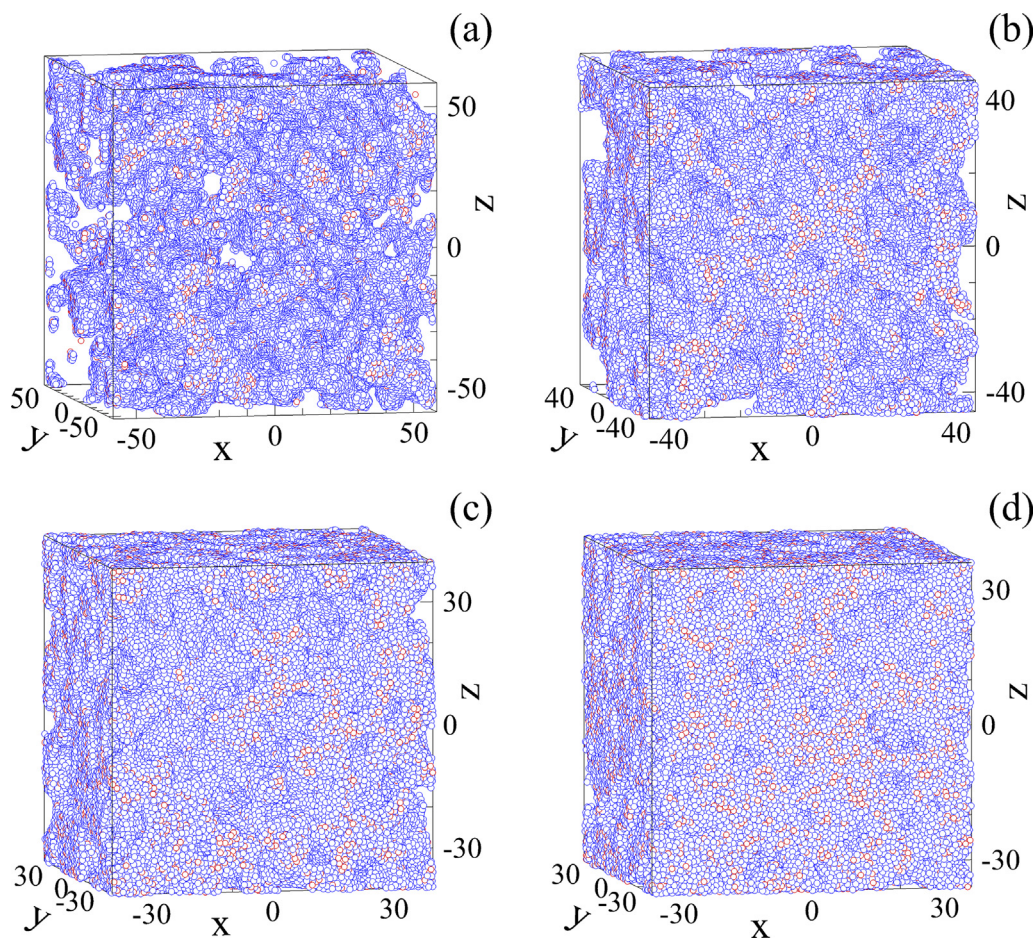


Fig. 1. Atom positions in the porous binary glass after isochoric quench to the temperature $T = 0.05\epsilon/k_B$ for the average glass densities (a) $\rho\sigma^3 = 0.2$, (b) $\rho\sigma^3 = 0.4$, (c) $\rho\sigma^3 = 0.6$, and (d) $\rho\sigma^3 = 0.8$. The blue and red circles indicate atom types A and B. The total number of atoms is $N = 300,000$. Note that atoms are not drawn to scale and the system sizes are different in all panels. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

solids [22]. However, the combination of several factors including the processing routes, system size and aspect ratio as well as surface defects and local microstructure makes it difficult to predict accurately the failure mode in strained glasses.

A few years ago, the phase separation kinetics of a glass-forming system quenched rapidly from a liquid state to a temperature below the glass transition was studied via molecular dynamics simulations [23,24]. As a result of the coarsening process at constant volume, a porous amorphous solid is formed, whose porous structure contains isolated voids at higher average glass densities and complex interconnected void-space topologies at lower glass densities [23,24]. More recently, the distributions of pore sizes and local glass densities were further investigated as a function of temperature and average glass density [25]. In particular, it was found that in systems with high porosity, the pore size distribution functions obey a scaling relation up to intermediate length scales, while in highly dense systems, the distribution is nearly Gaussian [25]. Furthermore, under steady shear deformation, the pores become significantly deformed and, at large strain, they were shown to aggregate into large voids that are comparable with the system size [26,27]. It was also demonstrated that the shear modulus follows a power-law dependence as a function of the average glass density [27]. Nevertheless, the mechanical response of porous glasses to different types of loading conditions and the evolution of porous structure during deformation remain not fully understood yet.

In this paper, molecular dynamics simulations are carried out to investigate the pore size distribution and mechanical properties of a model glass under tensile deformation. The porous glass is prepared via

a deep quench of a binary mixture in a liquid state to a very low temperature at constant volume. It will be shown that under tension, the distribution of pore sizes becomes highly skewed towards larger values, and upon further increasing strain, one large dominant pore is formed in the region where failure occurs. The analysis of local density profiles and visualization of atomic configurations reveals that the location of the failure zone is correlated with the extent of a lower glass density region.

The rest of the paper is structured as follows. In the next section, we describe the details of molecular dynamics simulations including model parameters as well as the equilibration and deformation protocols. The results for the stress–strain response, evolution of density profiles and pore size distributions are presented in Section 3. A brief summary and outlook are given in the last section.

2. Details of molecular dynamics simulations

The mechanical properties of porous glasses were investigated using the standard Kob-Andersen (KA) binary (80:20) mixture model [28]. In this model, the interaction between any two atoms are described via the Lennard-Jones (LJ) potential:

$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right], \quad (1)$$

where the parameters are set to $\epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\epsilon_{BB} = 0.5$, $\sigma_{AB} = 0.8$, $\sigma_{BB} = 0.88$, and $m_A = m_B$ [28]. For computational efficiency, the LJ forces were only computed at distances smaller than the cutoff radius

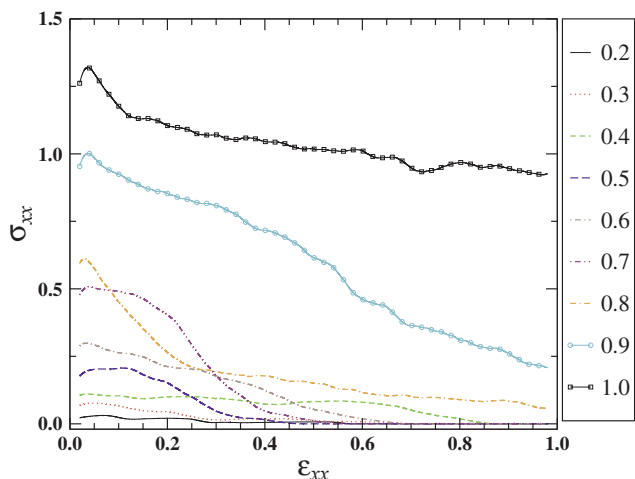


Fig. 2. The dependence of stress σ_{xx} (in units of $\varepsilon\sigma^{-3}$) as a function of strain for the average glass densities $\rho\sigma^3 = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0 (from bottom to top). The strain rate is $\dot{\varepsilon}_{xx} = 10^{-4}\tau^{-1}$ and temperature is $T = 0.05\varepsilon/k_B$.

$r_{c,\alpha\beta} = 2.5\sigma_{\alpha\beta}$. In what follows, the LJ units of length, mass, energy, and time are $\sigma = \sigma_{AA}$, $m = m_A$, $\varepsilon = \varepsilon_{AA}$, and, consequently, $\tau = \sigma\sqrt{m/\varepsilon}$. The equations of motion were solved numerically using the Verlet algorithm [30], implemented in LAMMPS [29], with the time step $\Delta t_{MD} = 0.005\tau$.

Our model porous systems were prepared by first equilibrating $N = 300,000$ atoms in a cubic cell at the temperature of $1.5\varepsilon/k_B$ during $3 \times 10^4\tau$, while keeping the volume constant. Here, k_B denotes the Boltzmann constant. For reference, the computer glass transition temperature of the KA model is $T_g \approx 0.435\varepsilon/k_B$ [28]. Second, the temperature of the liquid phase was instantaneously set to the low value of $0.05\varepsilon/k_B$, and the system was evolving during the time interval $10^4\tau$ at constant volume. During this process, the temperature of $0.05\varepsilon/k_B$ was maintained by simple velocity rescaling. Examples of the resulting porous structures are presented in Fig. 1 for the average glass densities $\rho\sigma^3 = 0.2, 0.4, 0.6$ and 0.8 . The equilibration and quenching procedures were performed for the average glass densities in the range $0.2 \leq \rho\sigma^3 \leq 1.0$, and the data were averaged over five independent samples for each value of $\rho\sigma^3$. For reference, the corresponding set of volumes V/σ^3 is: 1500000, 1000000, 750000, 600000, 500000, 428571.4, 375000, 333333.3, 300000. The dynamical evolution of the systems thus takes place at constant average density in both high and low (below the glass transition) temperature regimes. In the regime of ‘aging’, the systems were evolved during $10^4\tau$, as noted above. The above procedure is consistent with preparation protocols suggested in Refs. [23,24].

As detailed above, the atomic configurations for mechanical testing were prepared by thorough equilibration of the specimen using NVT simulations. In the next step, the porous samples were strained along the \hat{x} direction by rescaling the length of the simulation box. The constant strain rate $\dot{\varepsilon}_{xx} = 10^{-4}\tau^{-1}$ was used throughout the loading procedure. The deformation takes place during the time interval of $10^4\tau$ at the temperature of $0.05\varepsilon/k_B$, which is regulated by the Nosé-Hoover thermostat [29]. In nonequilibrium simulations, all stress components and system dimensions were saved every 0.5τ as well as atomic configurations that were stored every 500τ . These data were analyzed in five independent samples for each value of the average density, and used to compute the pore size distribution, density profiles, and the elastic modulus. The results are presented in the next section.

3. Results

It was recently demonstrated that, when a glass-forming system is rapidly quenched at constant volume from a high-temperature liquid state to a temperature below the glass transition point, the porous

structures are developed at sufficiently low average glass densities and fast cooling rates [23,24]. In the previous MD studies, the distribution of pore sizes and local densities of the solid phase [25] as well as temporal evolution of pore sizes and mechanical properties of systems under steady shear [27] were investigated in a wide range of the average glass densities, $0.2 \leq \rho\sigma^3 \leq 1.0$. The quiescent samples were prepared following the preparation procedure, described in Section 2. In Fig. 1, we show the representative snapshots of the porous samples before deformation for the average glass densities $\rho\sigma^3 = 0.2, 0.4, 0.6$ and 0.8 . It can be observed that at higher glass densities $\rho\sigma^3 \gtrsim 0.6$, the porous structure involves isolated voids with various sizes up to several molecular diameters, while at lower densities, the average size of pores increases and they become more interconnected, with channels running through the systems. Notice that at the lowest glass density $\rho\sigma^3 = 0.2$ in Fig. 1 (a), there are a number of straight paths across the whole sample, indicating that the porous network is above the percolation threshold.

The formation of porous glass occurs at a constant volume, and, therefore, the systems undergo evolution under the condition of negative pressure [31,32]. This has a number of important implications for the thermodynamic states of the porous glassy systems. First, the systems under consideration exist in metastable states. Also note that these systems can be envisaged as effectively confined [31,32]. Therefore, there exists a distribution of built-in tensile stresses in the solid domains of each phase-separating system. Correspondingly, the effects due to these stress distributions are expected to contribute to the dynamical evolution of the systems under mechanical loading; *i.e.*, when the thermodynamic barriers are perturbed by an applied external load. As was discussed in Ref. [25], the phase separation during the transition from liquid phase to that of porous glass occurs such that an extended high-density domains are formed in the systems. In the process of elongation (tension), a further phase separation can be made possible due to lowering of the corresponding thermodynamic barriers. Thus, the expected behavior is a redistribution of material from the region close to the failure zone to remote domains. In some cases, this process can be accompanied by pore shrinkage and/or closure. That is what we observed in the present study, as is detailed below. These strain-induced changes in porous structure lead to a significant decrease in built-in stresses.

The typical stress-strain curves are plotted in Fig. 2 for $\varepsilon_{xx} \leq 1.0$ and $0.2 \leq \rho\sigma^3 \leq 1.0$. The data are extracted from one sample for each value of the average glass density $\rho\sigma^3$. In our study, the tensile deformation along the \hat{x} direction was performed at a computationally slow strain rate $\dot{\varepsilon}_{xx} = 10^{-4}\tau^{-1}$ while keeping the volume constant. Thus, at the end of the deformation process, the original cell size in the \hat{x} direction, L_x , increases by a factor of two when $\varepsilon_{xx} = 1.0$. As shown in Fig. 2, the stress, σ_{xx} , at zero strain is finite, and its magnitude increases at higher densities. This behavior is consistent with the results of previous MD study, where the effects of temperature and average glass density on negative pressure in porous systems at equilibrium were thoroughly investigated [25]. In particular, it was shown that pressure is a strong function of the average density at low temperatures, and the data for different densities are well described by the scaling relation $P/T \sim \rho^\alpha$ [25].

At the initial stage of tensile deformation, $\varepsilon_{xx} \lesssim 0.04$, the stress increases for each value of the average glass density until it acquires a distinct maximum at the yield strain (see Fig. 2). Upon further increasing strain, $\varepsilon_{xx} \gtrsim 0.04$, the stress gradually decreases down to zero in porous systems with smaller average density, indicating material’s failure and breaking up into separate domains (discussed below). An enlarged view of the stress–strain curves at small strain is shown in Fig. 3. It can be seen that the tensile stress, σ_{xx} , is a linear function of strain for $\varepsilon_{xx} \lesssim 0.01$, and the slope, or the elastic modulus, increases at higher glass densities. In the inset to Fig. 3, the elastic modulus, E , averaged over five independent samples at each $\rho\sigma^3$, is plotted as a function of the average glass density. The results of our study show that the data are well described by the power-law function, $E \sim \rho^{2.41}$ (see the

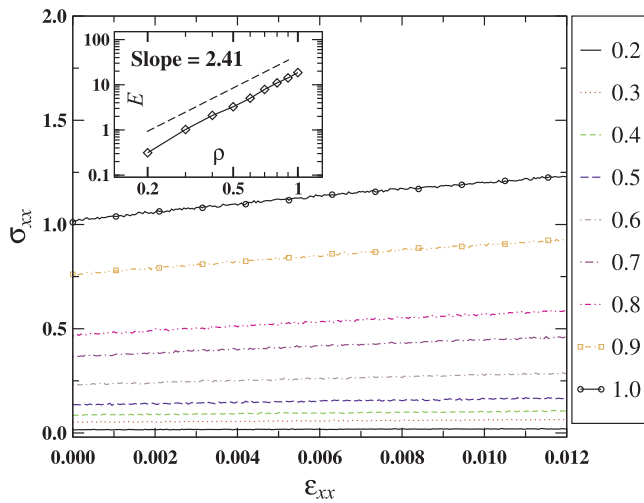


Fig. 3. The enlarged view of the stress-strain curves at strain $\epsilon_{xx} \lesssim 0.012$ and $\rho\sigma^3 = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0 (from bottom to top). The same data as in Fig. 2. The inset shows the elastic modulus E (in units of $\epsilon\sigma^{-3}$) versus the average glass density $\rho\sigma^{-3}$. The straight dashed line denotes the slope of 2.41.

dashed line in the inset to Fig. 3). It should be emphasized that the same exponent of 2.41 was reported for the dependence of the shear modulus versus glass density of porous samples under steady shear [27]. We also comment that the slopes of the stress–strain curves, shown in Fig. 3 remain the same at small negative values of strain during compression deformation (not shown).

The evolution of the porous structure during tensile deformation is illustrated in Figs. 4–6 for samples with $\rho\sigma^3 = 0.3, 0.5$ and 0.8 . In all

cases, it is evident that with increasing strain, the pore shapes become highly distorted, resulting ultimately in the formation of a single large void that separates solid domains. It can be observed that in the highly strained sample with the density $\rho\sigma^3 = 0.8$, shown in Fig. 6(d), the pores are essentially absent in the bulk glass due to compression along the lateral dimensions. Furthermore, the finite value of tensile stress at large strain $\epsilon_{xx} \approx 1.0$ for $\rho\sigma^3 = 0.8$ in Fig. 2 is associated with formation of the extended neck connecting solid domains shown in Fig. 6(d). Notice also in Fig. 4 that the sample with the density $\rho\sigma^3 = 0.3$ contains a number of small isolated clusters of atoms in the sparse network due to the finite cutoff radius of the LJ potential. The transformation of pore shapes in strained glasses can be more easily detected by visual inspection of a sequence of atomic configurations in thin slices of 10σ presented in Figs. 7–9. A more quantitative description of the distribution of void space can be obtained by counting a number of spheres of different sizes that can be inserted into the porous structure.

In our numerical analysis, the pore size distribution (PSD) functions were computed using the ZEO++ software [6,33,34]. The pore sizes were evaluated using the following computational approach. First, a decomposition of the system volume into Voronoi cells, associated with each individual atom, was performed. The void space geometry and topology characterization is based on a mapping between network of Voronoi nodes associated with each atom in the simulation systems and void space. The Voronoi decomposition is performed such that the space surrounding atoms is divided into polyhedral cells with their faces located on the planes equidistant from the two atoms sharing the face. Vertices of cells are the Voronoi nodes and they are equidistant from neighboring atoms. The Voronoi network, built of such nodes and edges represents the void space surrounding atoms in a periodic simulation cell. Analysis of such a network using Dijkstra-type graph algorithm makes it possible to detect subnetworks accessible to a probe

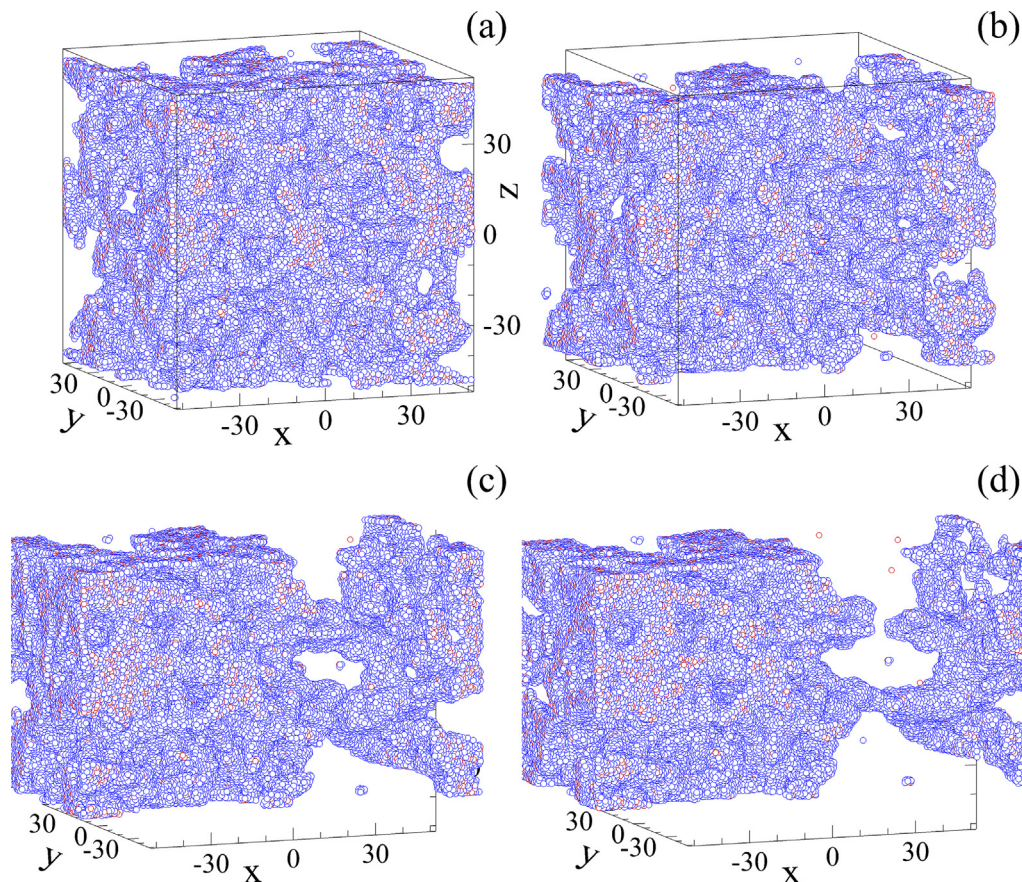


Fig. 4. Instantaneous atom positions for the average glass density $\rho\sigma^3 = 0.3$ and strain (a) $\epsilon_{xx} = 0.05$, (b) $\epsilon_{xx} = 0.25$, (c) $\epsilon_{xx} = 0.45$, and (d) $\epsilon_{xx} = 0.60$. The strain rate is $\dot{\epsilon}_{xx} = 10^{-4} \tau^{-1}$.

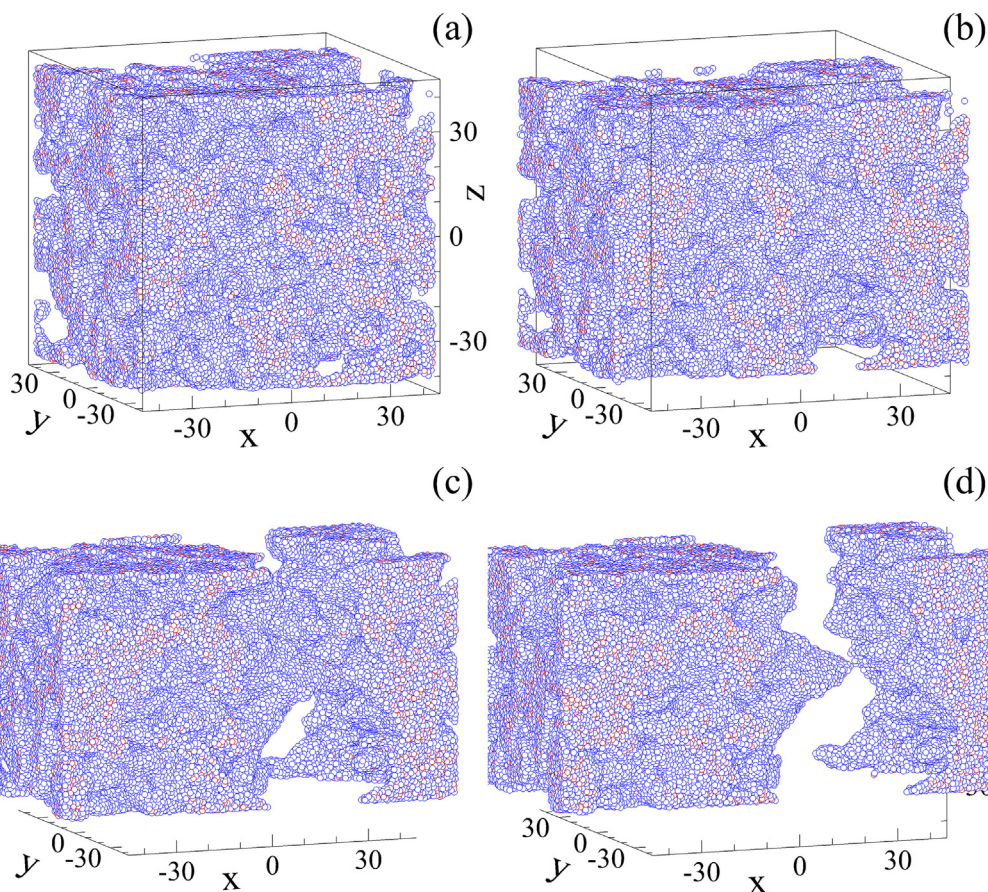


Fig. 5. A sequence of atomic configurations for the average glass density $\rho\sigma^3 = 0.5$ and strain values (a) $\epsilon_{xx} = 0.05$, (b) $\epsilon_{xx} = 0.25$, (c) $\epsilon_{xx} = 0.45$, and (d) $\epsilon_{xx} = 0.60$.

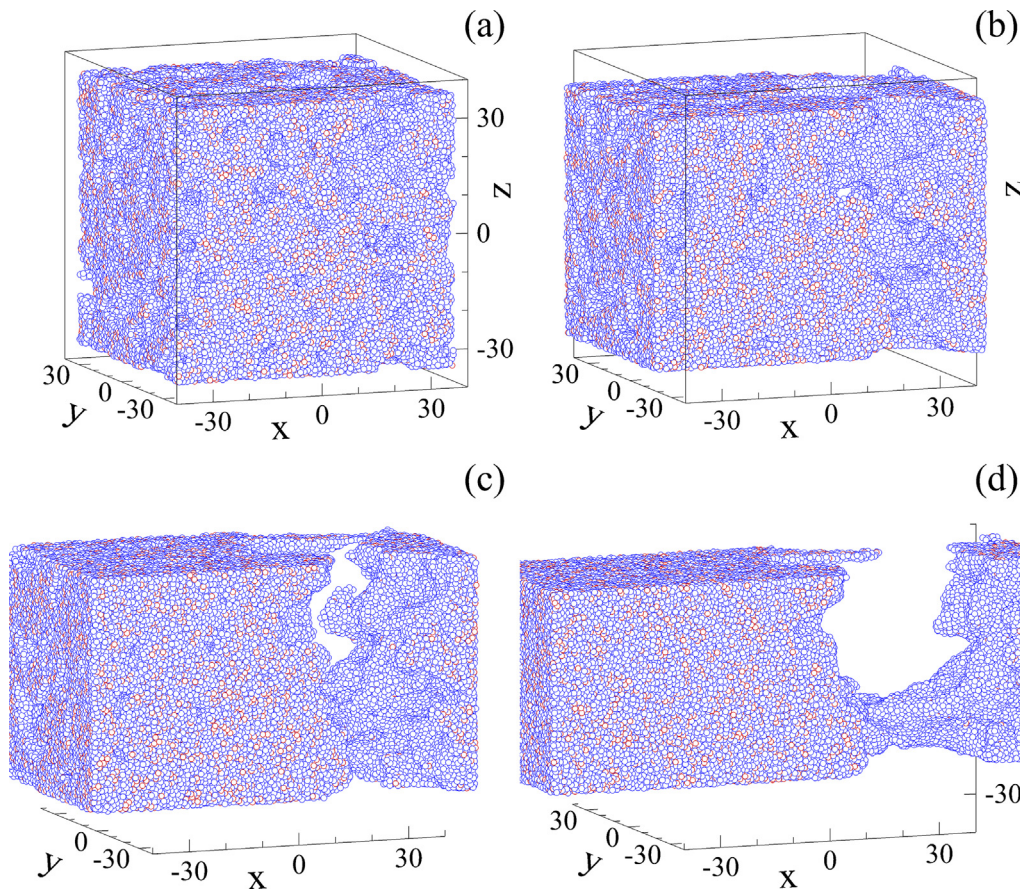


Fig. 6. Snapshots of atom positions for the average glass density $\rho\sigma^3 = 0.8$ and strain (a) $\epsilon_{xx} = 0.05$, (b) $\epsilon_{xx} = 0.25$, (c) $\epsilon_{xx} = 0.45$, and (d) $\epsilon_{xx} = 0.95$.

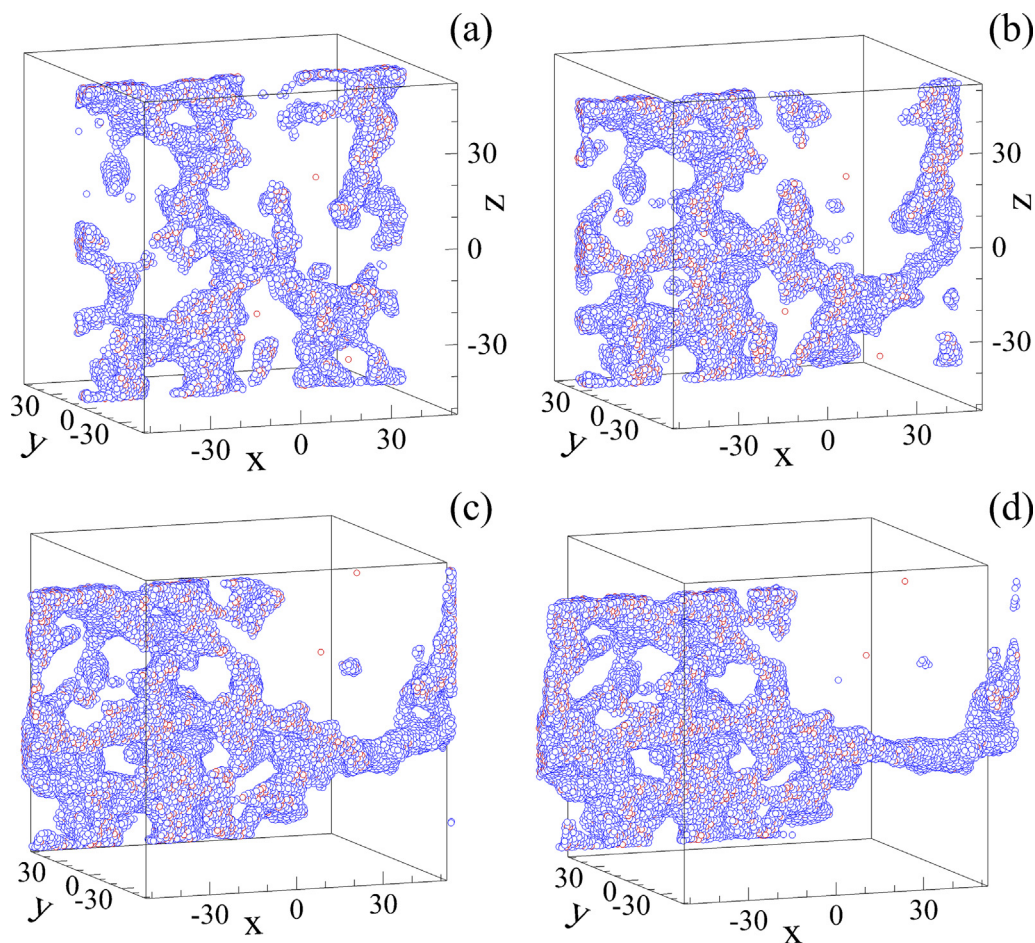


Fig. 7. Atom configurations within a slice of thickness 10σ for the average glass density $\rho\sigma^3 = 0.3$ and strain (a) $\epsilon_{xx} = 0.05$, (b) $\epsilon_{xx} = 0.25$, (c) $\epsilon_{xx} = 0.45$, and (d) $\epsilon_{xx} = 0.60$. Each panel contains a subset of the data shown in Fig. 4.

with given radius. Specifically, the algorithm is used to provide a three-dimensional representation of the pore-associated subnetworks and their connectivity. The implementation of the numerical method is based on a variation of the Dijkstra's shortest-path algorithm [35].

The pore size distribution functions, $\Phi(d_p)$, are presented in Fig. 10 for the average glass densities $\rho\sigma^3 = 0.3, 0.5$ and 0.8 . In agreement with the results of our previous study [25], the distribution of pore sizes in quiescent samples is narrow at high glass densities and it becomes broader as the average glass density decreases. The specifics of PSDs for porous binary glasses at equilibrium were previously discussed by the authors in Ref. [25]. Subsequently, the temporal evolution of PSDs in porous glasses undergoing steady shear were thoroughly investigated in Ref. [27]. Similar to the case of a simple shear [27], under small strain deformation, $\epsilon_{xx} = 0.05$, the shape of PSD curves remains largely unaffected (see Fig. 10). With increasing strain, the PSDs widen and start to develop a double-peak shape. In the regions of smaller d_p , the magnitude of PSDs decrease drastically, while the magnitudes of peaks, developed at larger values of d_p , increase. This type of behavior was also observed in porous glasses under shear [27]. In the case of tension, however, this effect is significantly amplified in the case of $\rho\sigma^3 = 0.8$. Indeed, the small-size pores nearly disappear, when ϵ_{xx} exceeds ≈ 0.5 . Also, in the limit of extremely large strains ($\epsilon_{xx} \rightarrow 1.0$), the double peak structure disappears and a single peak of large magnitude develops instead. Overall, these conclusions are similar to the case of shearing and can be summarized as follows. Tensile loading induces deformation and coalescence of compact pores into larger voids that ultimately lead

to the formation of system-spanning empty regions associated with breaking of samples into two pieces. The process of large pores formation is consistent with series of system snapshots shown in Figs. 4–9, where the material's failure is accompanied by pore redistribution into larger domains and with densification of the solid parts.

The evolution of the pore-size distributions with applied strain during mechanical loading is important for overall understanding response properties of porous materials. However, as any average quantity, they do not provide any spatially-resolved information on the dynamic events in material systems under loading. In what follows, we therefore augment the PSDs by the analysis of spatially-resolved density profiles. Specifically, we consider locally averaged density, computed along the direction of mechanical loading, $\langle \rho \rangle_s(x)$. This quantity is defined as the number of atoms located in a thin slice of thickness σ along the \hat{x} direction (i.e., the direction of mechanical loading), divided by the volume of the slice: $L_y L_z \sigma^3$, where L_y and L_z are the system sizes in the two Cartesian directions perpendicular to the loading direction.

The temporal evolution of the average density profiles in porous samples is illustrated in Figs. 11–13. Here, we present the results for systems with reduced densities, $\rho\sigma^3$, of $0.3, 0.5$, and 0.8 . First and foremost, we would like to emphasize one common feature, which is characteristic of all the samples, we studied in this work. It regards the location of the zone, where the material's failure occurs. As seen in Figs. 11–13, it appears that the location of the failure zone is correlated with the low-density region. However, a deeper analysis suggests that

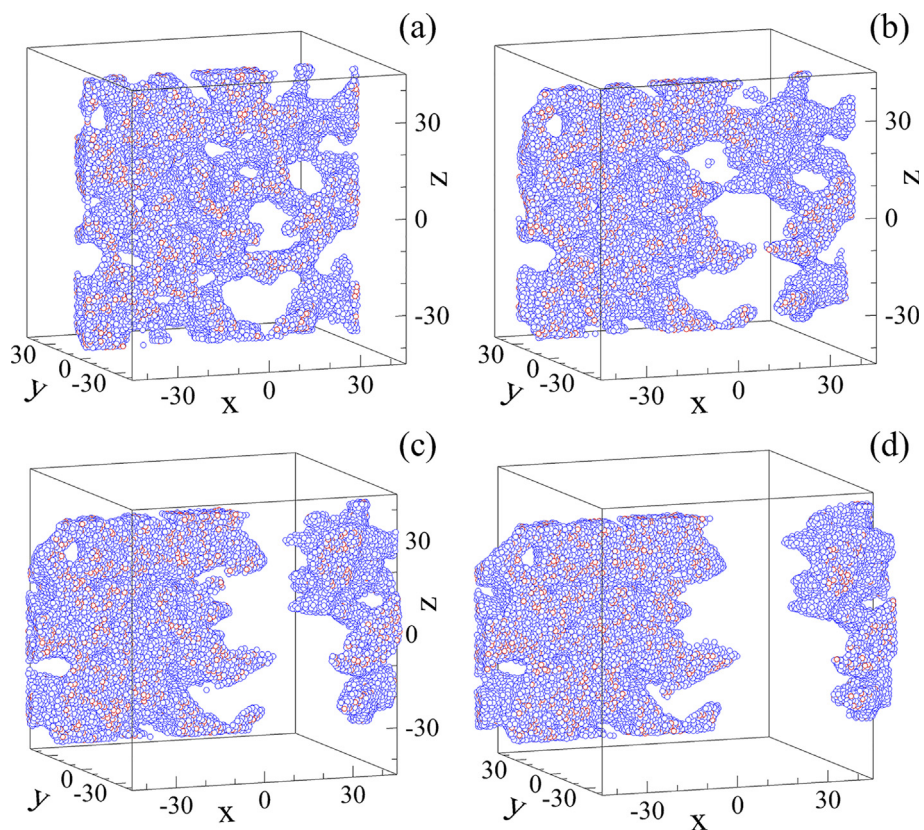


Fig. 8. Atom positions within the narrow slice of 10σ for the average glass density $\rho\sigma^3 = 0.5$ and strain (a) $\epsilon_{xx} = 0.05$, (b) $\epsilon_{xx} = 0.25$, (c) $\epsilon_{xx} = 0.45$, and (d) $\epsilon_{xx} = 0.60$. The same data as in Fig. 5.

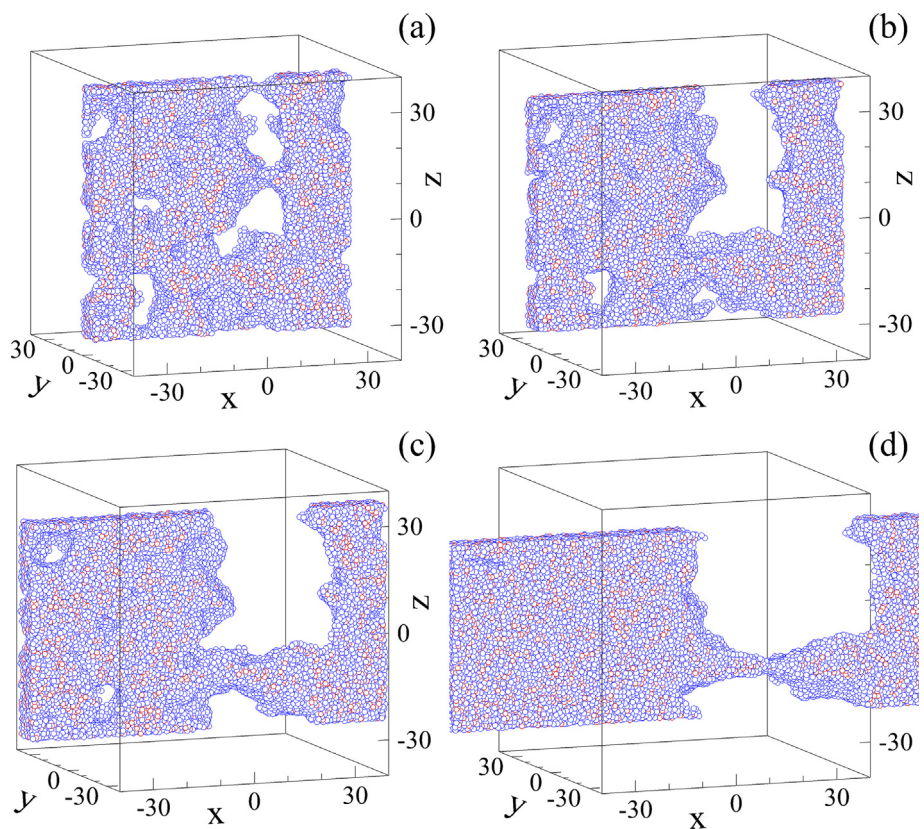


Fig. 9. Snapshots of the porous glass in a thin slice of 10σ for the average glass density $\rho\sigma^3 = 0.8$ and strain (a) $\epsilon_{xx} = 0.05$, (b) $\epsilon_{xx} = 0.25$, (c) $\epsilon_{xx} = 0.45$, and (d) $\epsilon_{xx} = 0.95$. The same data set as in Fig. 6.

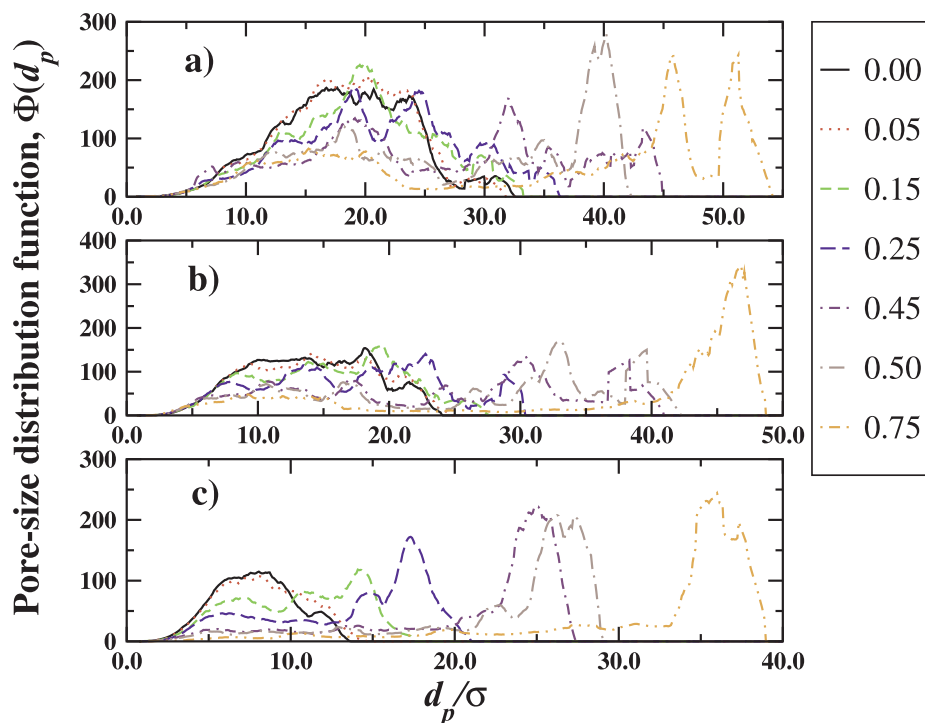


Fig. 10. The distribution of pore sizes for the average glass densities (a) $\rho\sigma^3 = 0.3$, (b) $\rho\sigma^3 = 0.5$, and (c) $\rho\sigma^3 = 0.8$. The distribution functions at different strains are indicated by solid black curves ($\varepsilon_{xx} = 0.0$), dotted red curves ($\varepsilon_{xx} = 0.05$), dashed green curves ($\varepsilon_{xx} = 0.15$), dashed blue curves ($\varepsilon_{xx} = 0.25$), dash-dotted velvet curves ($\varepsilon_{xx} = 0.45$), dash-dotted brown curves ($\varepsilon_{xx} = 0.50$), double-dot-dashed orange curves ($\varepsilon_{xx} = 0.75$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the defining factor is *the spatial extent of such a region*, rather than the absolute value of local density deviation from the average value. The failure takes place in the regions of largest spatial extent of local density deviations from the average value. In other words, a local deviation of density from its average in a narrow spatial region does not signify a weak (from a structural mechanics' perspective) region. Rather, the failure takes place in the center of extended low-density zone.

This is evident in all three cases of the average glass density presented in Figs. 11–13. Indeed, at strains around 0.1, a dip in $\langle \rho \rangle_s(x)$ starts to develop within the regions with low average densities. The process of local density decrease in these regions is accompanied by simultaneous densification in the neighboring parts of the systems. Note that shapes of the density patterns are largely preserved in the remote - from the regions with large paucity - parts of the systems. In loose terms, one can say that the patterns repeat themselves, the only difference being their magnitudes and lateral shifts, taking place due to gradual increase in the extent of the low-density region. Within each low-density region, in the initial stages of loading, the density profile shows a rather sharp dip. In the later stages, the profiles show the characteristic for interfacial regions (hyperbolic-tangent like) shapes. Note also that in Figs. 11–13, the density profiles are plotted as functions of scaled (to the evolving system size) coordinates. This may create an illusion that the positions of the failure regions are similar for all the samples. However, as our analysis shows, both the shapes of the failure regions and their positions vary from sample to sample.

We finally comment that the process of density evolution is gradual; *i.e.*, no abrupt transitions between density states were observed. The cases of strains $\varepsilon_{xx} = 0$ and 0.05 as well as $\varepsilon_{xx} = 0.45$ and 0.50 in Figs. 11–13 provide an illustration of the premise in the initial and intermediate stages of loading, correspondingly. Upon failure, the samples with high densities exhibit some density relaxation on both

sides of the failure region. This is because a part of the tensile energy, supplied in the process of external loading, is stored in the dense parts of the system. This conclusion follows from the temporal behavior of the systems after failure. The two parts continue to densify after break-up, as evident from the behavior of systems with $\rho\sigma^3 = 0.3$ and 0.5 shown in Figs. 11 and 12, respectively. In the case of system with high densities (see $\rho\sigma^3 = 0.8$) the effects is less pronounced. Note, however, the behavior in the region around density dip, located at $x/L_x \sim 0.22$, in Fig. 13. There is clear sign of continued relaxation due to elastic energy, accumulated during the loading. The magnitude of the effects is expected to be smaller, as structural rearrangement in a high-density material requires more energy, as compared to its low-density counterparts.

4. Conclusions

In summary, the mechanical response and evolution of porous structure in binary glasses under tension were studied using molecular dynamics simulations. The phase separating glassy systems were prepared via rapid quench from a liquid state to a temperature well below the glass transition. In the process of phase separation at constant volume, different pore topological structures are formed depending on the average glass density. Visual inspection of system snapshots in the absence of deformation shows atom configurations with randomly distributed, isolated pores at higher average glass densities, while interconnected porous structure is formed at lower densities. These structural changes are reflected in the shape of pore size distribution functions computed at different average glass densities.

When the porous material is subjected to tensile loading at constant volume, the stress–strain curves exhibit a linear regime, where the absolute value of stress increases up to the yield point, and then

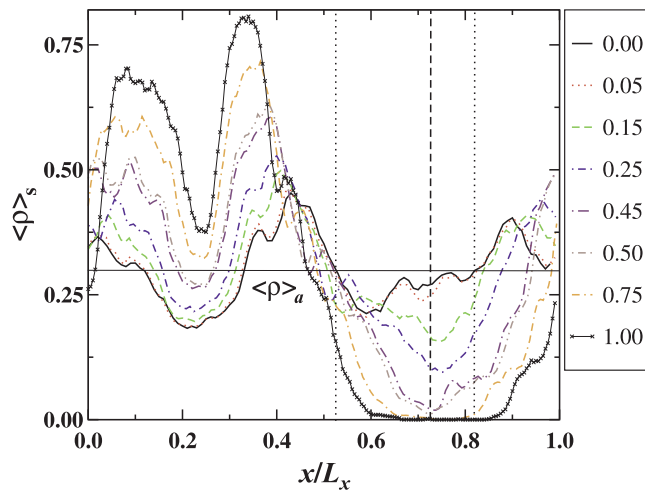


Fig. 11. The density profiles $\langle \rho \rangle_s(x)$ (in units of σ^{-3}) for the values of strain $\varepsilon_{xx} = 0.0$ (solid black curve), 0.05 (dotted red curve), 0.15 (dashed green curve), 0.25 (dash-dotted blue curve), 0.45 (dash-dotted violet curve), 0.5 (dash-double-dotted brown curve), 0.75 (dash-dotted orange curve), and 1.0 (black curve with crosses). The data were averaged in one sample in thin slices parallel to the yz plane. The horizontal blue line indicates the average glass density $\rho\sigma^3 = 0.3$. The two vertical dotted lines mark the borders of the region with reduced density. The dashed vertical line shows the position of the failure zone center. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

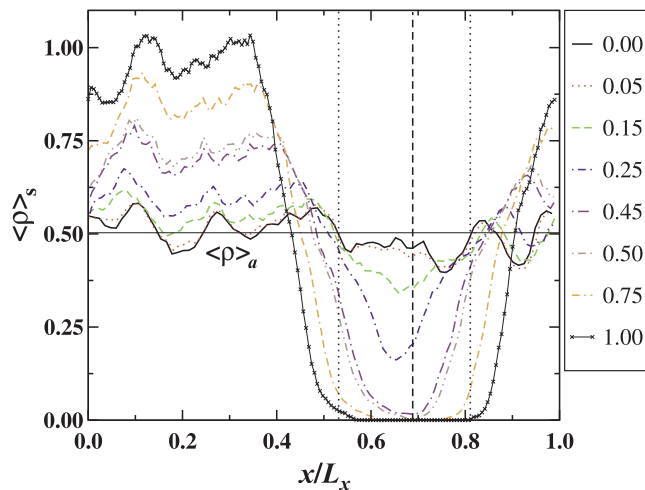


Fig. 12. The atomic density profiles $\langle \rho \rangle_s$ (in units of σ^{-3}) along the \hat{x} axis for the same values of strain as in Fig. 11. The average glass density $\rho\sigma^3 = 0.5$ is indicated by the horizontal blue line. The colorcode is the same as in Fig. 11. The strain values are listed in the legend. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

followed by plastic deformation at large strain until failure. Consistently with theoretical predictions, the power-law exponent of the elastic modulus dependence on the average glass density is the same as for the shear modulus of porous glasses reported in our previous study [27]. Upon further loading, the pores become significantly deformed and redistributed spatially, thus forming a system-spanning void associated with breaking of the amorphous material. The analysis of the locally averaged density profiles elucidates the mechanism of the failure mode, which originates in regions of lower glass density of largest spatial extents.

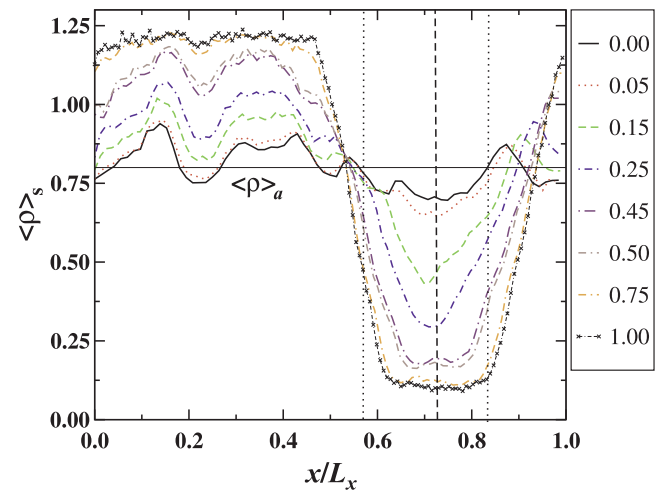


Fig. 13. The averaged density profiles $\langle \rho \rangle_s(x)$ (in units of σ^{-3}) for selected values of strain. The average glass density is $\rho\sigma^3 = 0.8$. The colorcode and strain values are the same as in Figs. 11 and 12. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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References

- [1] M.M. Porter, R. Imperio, M. Wen, M.A. Meyers, J. McKittrick, Bioinspired scaffolds with varying pore architectures and mechanical properties, *Adv. Funct. Mater.* 24 (2014) 1978.
- [2] Y. Li, Z.-Y. Fu, B.-L. Su, Hierarchically structured porous materials for energy conversion and storage, *Adv. Funct. Mater.* 22 (2012) 4634.
- [3] J. Zhang, H. Zhou, K. Yang, Y. Yuan, C. Liu, RhBMP-2-loaded calcium silicate/calcium phosphate cement scaffold with hierarchically porous structure for enhanced bone tissue regeneration, *Biomaterials* 34 (2013) 9381.
- [4] E.C. Hammel, O.L.-R. Ighodaro, O.I. Okoli, Processing and properties of advanced porous ceramics: an application based review, *Ceram. Int.* 40 (2014) 15351.
- [5] Q. Fu, E. Saiz, A.P. Tomsia, Bioinspired strong and highly porous glass scaffolds, *Adv. Funct. Mater.* 21 (2011) 1058.
- [6] D. Ongari, P.G. Boyd, S. Barthel, M. Witman, M. Haranczyk, B. Smit, Accurate characterization of the pore volume in microporous crystalline materials, *Langmuir* 33 (2017) 14529.
- [7] B. Sarac, B. Klusemann, T. Xiao, S. Bargmann, Materials by design: an experimental and computational investigation on the microanatomy arrangement of porous metallic glasses, *Acta Mater.* 77 (2014) 411.
- [8] B. Sarac, D. Soppa, E. Park, J.K. Hufenbach, S. Oswald, M. Stoica, J. Eckert, Mechanical and structural investigation of porous bulk metallic glasses, *Metals* 5 (2015) 920.
- [9] D. Soppa, C. Soyarslan, B. Sarac, S. Bargmann, M. Stoica, J. Eckert, Structure-property relationships in nanoporous metallic glasses, *Acta Mater.* 106 (2016) 199.
- [10] Y.-C. Chen, Z. Lu, K. Nomura, W. Wang, R.K. Kalia, A. Nakano, P. Vashishta, Interaction of voids and nanoductility in silica glass, *Phys. Rev. Lett.* 99 (2007) 155506.
- [11] J.M. Rimsza, J. Du, Structural and mechanical properties of nanoporous silica, *J. Am. Ceram. Soc.* 97 (2014) 772.
- [12] Y. Shi, Size-independent shear band formation in amorphous nanowires made from simulated casting, *Appl. Phys. Lett.* 96 (2010) 121909.
- [13] F.L. Yuan, L.P. Huang, Molecular dynamics simulation of amorphous silica under uniaxial tension: From bulk to nanowire, *J. Non-Cryst. Solids* 358 (2012) 3481.
- [14] S. Adibi, P.S. Brancio, R. Lontas, D.Z. Chen, J.R. Greer, D.J. Srolovitz, S.P. Joshi, Surface roughness imparts tensile ductility to nanoscale metallic glasses, *Extreme*

- Mech. Lett. 5 (2015) 88.
- [15] D. Sopy, A. Foroughi, M. Stoica, J. Eckert, Brittle-to-ductile transition in metallic glass nanowires, *Nano Lett.* 16 (2016) 4467.
- [16] Q. Zhang, Q.-K. Li, M. Li, Key factors affecting mechanical behavior of metallic glass nanowires, *Sci. Rep.* 7 (2017) 41365.
- [17] H. Guo, P.F. Yan, Y.B. Wang, J. Tan, Z.F. Zhang, M.L. Sui, E. Ma, Tensile ductility and necking of metallic glass, *Nat. Mater.* 6 (2007) 735.
- [18] D.Z. Chen, D. Jang, K.M. Guan, Q. An, W.A. Goddard, J.R. Greer, Nanometallic glasses: size reduction brings ductility, surface state drives its extent, *Nano Lett.* 13 (2013) 4462.
- [19] D.J. Magagnosc, R. Ehrbar, G. Kumar, M.R. He, J. Schroers, D.S. Gianola, Tunable tensile ductility in metallic glasses, *Sci. Rep.* 3 (2013) 1096.
- [20] J. Yi, W.H. Wang, J.J. Lewandowski, Sample size and preparation effects on the tensile ductility of Pd-based metallic glass nanowires, *Acta Mater.* 87 (2015) 1.
- [21] D. Sopy, Y. Ritter, H. Gleiter, K. Albe, Deformation behavior of bulk and nanostructured metallic glasses studied via molecular dynamics simulations, *Phys. Rev. B* 83 (2011) 100202 R.
- [22] J. Ashwin, O. Gendelman, I. Procaccia, C. Shor, Yield-strain and shear-band direction in amorphous solids under two-dimensional uniaxial loading, *Phys. Rev. E* 88 (2013) 022310.
- [23] V. Testard, L. Berthier, W. Kob, Influence of the glass transition on the liquid-gas spinodal decomposition, *Phys. Rev. Lett.* 106 (2011) 125702.
- [24] V. Testard, L. Berthier, W. Kob, Intermittent dynamics and logarithmic domain growth during the spinodal decomposition of a glass-forming liquid, *J. Chem. Phys.* 140 (2014) 164502.
- [25] M.A. Makeev, N.V. Priezjev, Distributions of pore sizes and atomic densities in binary mixtures revealed by molecular dynamics simulations, *Phys. Rev. E* 97 (2018) 023002.
- [26] L. Di Michele, D. Fiocco, F. Varrato, S. Sastry, E. Eisera, G. Foffi, Aggregation dynamics, structure, and mechanical properties of bigels, *Soft Matter* 10 (2014) 3633.
- [27] N.V. Priezjev, M.A. Makeev, Evolution of the pore size distribution in sheared binary glasses, *Phys. Rev. E* 96 (2017) 053004.
- [28] W. Kob, H.C. Andersen, Testing mode-coupling theory for a supercooled binary Lennard-Jones mixture: the van Hove correlation function, *Phys. Rev. E* 51 (1995) 4626.
- [29] S.J. Plimpton, Fast parallel algorithms for short-range molecular dynamics, *J. Comp. Phys.* 117 (1995) 1.
- [30] M.P. Allen, D.J. Tildesley, *Computer Simulation of Liquids*, Clarendon, Oxford, 1987.
- [31] K. Adrjanowicz, K. Kaminski, K. Koperwas, M. Paluch, Negative pressure vitrification of the isochorically confined liquid in nanopores, *Phys. Rev. Lett.* 115 (2015) 265702.
- [32] M. Tarnacka, O. Madejczyk, K. Kaminski, M. Paluch, Time and temperature as key parameters controlling dynamics and properties of spatially restricted polymers, *Macromolecules* 50 (2017) 5188.
- [33] R.L. Martin, B. Smit, M. Haranczyk, Addressing challenges of identifying geometrically diverse sets of crystalline porous materials, *J. Chem. Inf. Model.* 52 (2012) 308.
- [34] T.F. Willems, C.H. Rycroft, M. Kazi, J.C. Meza, M. Haranczyk, Algorithms and tools for high-throughput geometry-based analysis of crystalline porous materials, *Micropor. Mesopor. Mater.* 149 (2012) 134.
- [35] E.W. Dijkstra, A note on two problems in connexion with graphs, *Numer. Math.* 1 (1959) 269.