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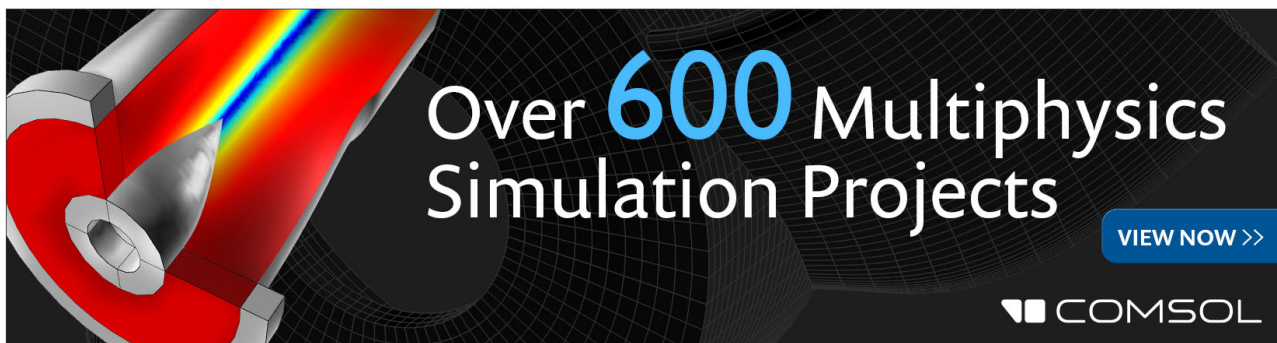
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Indicators of internal structural states for metallic glasses: Local order, free volume, and configurational potential energy

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The structural states of metallic glasses (MGs) have been described previously using concepts such as free volume and configurational potential energy. Here we discuss the inadequacy of these indicators by examining a Cu–Zr–Al MG model experiencing different cooling and relaxation history. The results identify the local (icosahedral) ordering as a fundamental process underlying structural relaxation, and the degree of order as a more sensitive and revealing structural indicator. © 2008 American Institute of Physics. [DOI: 10.1063/1.2966154]

Establishing the structure-property correlation is central to the science materials. For amorphous alloys, however, how the internal structure influences their properties is difficult to understand.¹ For example, the strength and plasticity of metallic glasses (MGs) can be strongly dependent on processing history, such as the different cooling rates used for making the MG and the aging/annealing treatment of the as-prepared glass.^{2,3} However, structurally, these MGs all appear completely amorphous. It is not obvious what the structural differences are that lead to major property variations.

There have been several models proposed over the years, introducing indicators that presumably can serve as a measure of the role glass structure plays in controlling properties.^{4–7} These indicators mainly fall into two categories. The first and foremost is the widely used concept of “free volume,”⁴ or a similar parameter of atomic packing efficiency/density.⁵ Alternatively, the structural state has been characterized using the configurational potential energy (CPE),⁶ or potential energy of inherent structures.⁷ However, such volumetric and energetic parameters are often inadequate for revealing the structural states and processes, as discussed below.

The free volume is defined as the atomic volume in excess of an ideally packed reference amorphous state.⁴ The original concept of free volume by Cohen and Turnbull⁸ was adopted by Spaepen⁴ to model the mechanical behavior of MGs. This approach has been shown to be very useful and hence enjoyed much popularity.⁹ However, this free volume indicator also has major drawbacks.⁹ For example, the free volume is not a tangible physical entity that can be quantitatively determined.¹⁰ One can measure molar volume and its changes,¹⁰ or sense excess volume from positron lifetime in positron annihilation measurements,¹¹ but to quantify the absolute value of free volume, one needs a reference state with predefined zero free volume. Here the use of either random dense packing, ideal glass, or nearby crystals is rather arbitrary and questionable.^{12,13} In fact, even if well defined, the ideal reference state is usually impossible to achieve in experiments.⁹ More importantly, the volume as a variable does not in itself contain information about the topological symmetry and chemically ordered local environment, both of which are critical for (multicomponent) MG properties. As a

thought experiment, one can picture a rearrangement of the atomic species and bonds in an MG, resulting in appreciable changes in properties but no obvious changes in the average free volume content.

From the potential energy landscape (PEL) perspective,¹⁴ the CPE,⁶ defined here as the local minimum position in the PEL, includes both the chemical and geometrical effects, and is a useful indicator of the state the glass structure is in. In fact, the CPE and the local profile of the PEL are directly related to the mechanical properties,^{6,15–17} with the implication that the configurational rearrangement in a glass can lead to major changes of properties. However, this CPE indicator does not provide a clear picture of the atomic-level structure, when the system changes its position in the PEL.

Also belonging to this category is the idea of effective/fictive temperature,¹⁸ defined as a measure of the degree of structural ordering in MGs. This temperature is a virtual concept for modeling, not a physically measurable quantity. Recent work by Shi *et al.* showed that the fictive temperature could be connected with the average local potential energy by a scaling factor.¹⁹ It is thus analogous to the CPE indicator above.

In this letter, we use a Cu₄₆Zr₄₇Al₇ (Ref. 20) MG model to show that the above volumetric and energetic indicators are not sufficiently sensitive and revealing for unraveling all the internal structure differences. Indicators monitoring the structural ordering are more direct and informative, and can account for the energy and property changes observed both in experiments²¹ and simulations.²² Short-range order in MGs has been extensively discussed before, but its quantitative characterization and monitoring in realistic bulk metallic glass structural models have not been possible.

Many-body interatomic interaction potentials employing the embedded atom method (EAM) formalism were developed for the Cu–Zr–Al system using the force-matching method,²³ by fitting the PEL surveyed via VASP (Ref. 24) *ab initio* simulations of over 500 atomic configurations, each typically consisting of 96–128 atoms, for crystalline, liquid, and glass phases. The generated EAM parameters were further refined using a recursive method and validated against a large set of experimental and *ab initio* data. The details of the potential development will be presented elsewhere.²² NPT ensembles of Cu₄₆Zr₄₇Al₇, containing 10 000 atoms with pe-

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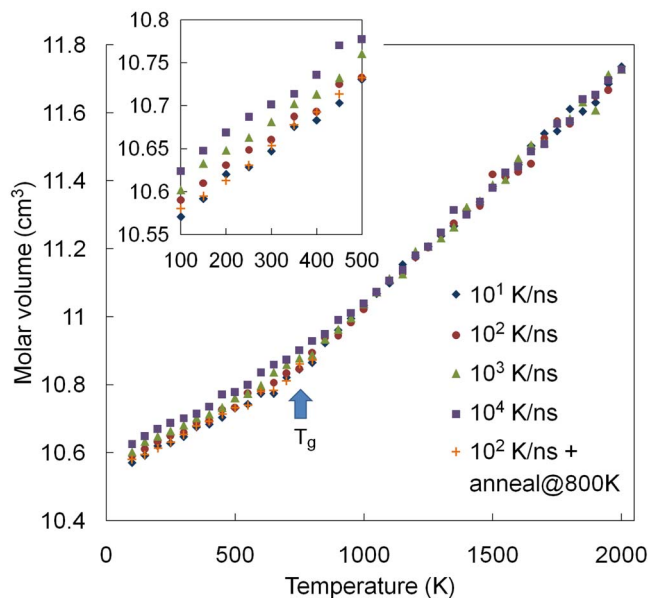


FIG. 1. (Color online) Evolution of molar volume with temperature during liquid quenching. The MD-annealed sample is included for comparison. Glass transition temperature (T_g , slightly different for different cooling rates) was estimated by MD simulation and marked by an arrow (the same for Figs. 2 and 3). Inset is an enlarged view showing the small differences of molar volume for MGs with different cooling history.

riodic boundary conditions, were melted and equilibrated at 2000 K for 2 ns (time step 2 fs), and cooled down to 100 K at four different cooling rates (10^4 – 10^1 K/ns). We also have samples annealed for 10 ns at 800 K, which were quenched at 10^2 K/ns before and after the annealing. These various MG samples exhibit different mechanical behavior under loading.²²

In Fig. 1, we see that the molar volume of the MGs (obtained from quenching the liquids) is larger at higher cooling rates. For a cooling rate change of one order of magnitude, the molar volume only changes by $\sim 0.1\%$. This insensitivity is consistent with the experimentally observed trend, when the cooling rate changes by several orders of magnitude (e.g., for MG prepared using melt spinning versus bulk MG made via copper mold casting), and also consistent with the estimate that free volume change is only a fraction of one percent of the total volume.¹⁰ This small volume change is not easy to measure accurately (large error margin in experiments), although its effects on the corresponding property could be significant, and hence not very convenient or effective to use for correlating structure with properties. We will also show later that the volume change is not the only, or even the major, evolution the structure experiences in relaxation.

Figure 2 shows the evolution of the CPE with temperature for various cooling history. It is seen that the quenched-in CPE of the MG is reduced with decreasing cooling rates, or increased structural relaxation (subsequent annealing/aging). The enthalpy release during structure relaxation measured in calorimetry scans^{25,26} has previously been used as an indirect measure of the free volume in the MG. However, the calorimetric enthalpy release is much larger than the energy reduction expected from the annihilation of vacancylike open volume,²⁵ pointing to sources other than the volume. A similar conclusion is reached for our model system. The average CPE reduction of ~ 5

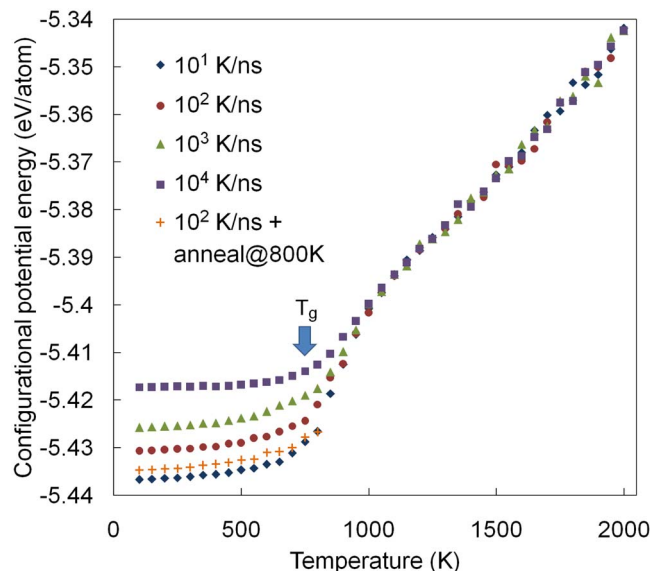


FIG. 2. (Color online) Evolution of CPE with temperature during quenching.

$\times 10^{-3}$ eV/atom (~ 500 J/mol), when we lower the cooling rate by one order of magnitude, cannot be attributed to the change in volume alone.^{25,26} As we show next, the volumetric indicator (Fig. 1) in fact misses important and large contributions to enthalpy, due to marked changes in local order during structural relaxation.

Now, exactly how does the atomic-level structure change, along with the subtle molar volume change and the more obvious change in CPE? Using Voronoi tessellation method and Voronoi indices as the characterization tool,²⁷ we found the local inherent structure to depend strongly on cooling history, in terms of the local order and symmetry reflected by the makeup of Voronoi polyhedra²⁷ around Cu and Al. Specifically, among all the Cu(Al)-centered coordination polyhedra, the fraction of the 12-coordinated $\langle 0,0,12,0 \rangle$ full icosahedra (although not perfect/ideal due to the different atomic sizes) with complete fivefold environment^{22,27} is found to be very sensitive to the cooling rate and relaxation history, while other types of polyhedra are not. Figure 3 shows the evolution of full coordination icosahedra at Cu (Al) sites during the various cooling schedules. The dependence of the fraction of full icosahedra on cooling history is remarkable. It doubles for the cooling rate range covered in these MD simulations. Upon quenching towards glass transition, the structural rearrangement (ordering) around the smaller species appears to be the dominant mechanism underlying structural development, along with only minor variations in molar volume. Note that for multicomponent MGs such as Cu-Zr-Al, the nearest neighbor shell necessarily consists of multiple atomic species with different sizes, so that differences in local order entail changes in both topological and chemical environment. The changing fraction of full icosahedra would thus reflect simultaneous changes in coordination number, polyhedra symmetry, as well as the number and distribution of various bonding species in the shell.

To observe the energy difference with increased relaxation, we can treat the total energy reduction as coming from two parts: one is due to the volume change, and the other is due to changes in the topological symmetry and chemical

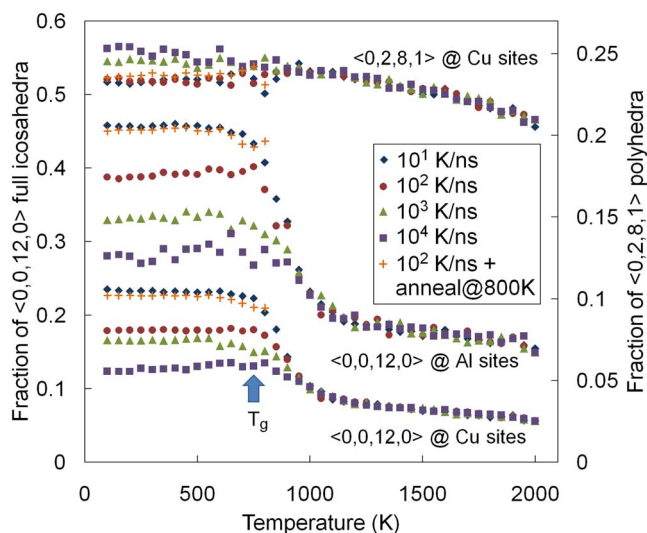


FIG. 3. (Color online) Evolution of $\langle 0,0,12,0 \rangle$ full icosahedra at Cu (Al) sites with temperature during quenching, showing the dramatic increase of full icosahedral ordering in the supercooled liquid region and its strong dependence on cooling history. For comparison, an example of $\langle 0,2,8,1 \rangle$ (see Ref. 27) at Cu sites is also shown (right y axis) to represent other types of polyhedra, which do not change markedly with cooling.

ordering. We annealed the sample at 800 K with two contiguous steps: an NVT (constant volume) annealing for 10 ns, followed by a simple scaling (shrinkage) of the box size to adjust the pressure to zero. The CPE reduction associated with NVT annealing is 4×10^{-3} eV/atom (similar amount of enthalpy release is typical of structural relaxation of glasses²⁵), and for the volume shrinkage it is only 5×10^{-4} eV/atom. This suggests that even without the volume change, the majority of the CPE reduction can still be realized through topological and chemical rearrangement (e.g., the fraction of full icosahedra at Cu sites increases from 17% to 20% in this step). The density increase alone is only a small contribution to the total CPE reduction. Therefore, under the constant pressure condition, it seems more appropriate to consider the volume change as a natural consequence of atomic rearrangement toward improved topological and chemical ordering. The volume decrease is neither the origin nor the prerequisite. It is not even the dominant factor responsible for the energy reduction. It is more like a side effect accompanying the more fundamental local topological and chemical environment changes.

Before summarizing, we note that due to the spatiotemporal limitations (e.g., the very high cooling rate) the MD simulation is not meant to quantitatively capture the real-world property values, but to provide microscopic insight. Figure 3 shows that the slower the cooling rate, the more the full icosahedral ordering. It is then natural to extrapolate that for laboratory-quenched glasses (with vapor quenching at rates similar to the ones used here, and liquid quench at much slower cooling rates) the full icosahedral ordering would be at least as much and in most cases more pronounced. Meanwhile, the holding or aging time in experiments is also much longer than the short anneal in simulation, allowing extensive relaxation. In all cases, however, the structural ordering scenario demonstrated above is expected to dominate the relaxation process.

In summary, using the $\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$ model for typical bulk metallic glasses we have demonstrated the strong de-

pendence of the structural order on the cooling rate (or relaxation history of the glass). This information is not included in less-revealing and less-sensitive structural indicators such as free volume and CPE, which have often been used previously to explain mechanical property variations. Moreover, we quantitatively compared different MG samples and showed that the development of improved local topological order and symmetry, as well as increased local chemical order, is the major structural relaxation process responsible for the reduction in CPE, whereas the annihilation of excess volume (small reduction in molar volume and increase in packing density) is actually only one manifestation and consequence of the structural rearrangement. The enthalpy release observed during relaxation in calorimetry experiment^{25,26} can be mainly due to structural ordering, and as such cannot be simply interpreted as a measure of the free volume.^{25,26} The varying degree of structural order can in fact be the primary structural origin of the mechanical property differences, as investigated elsewhere.^{5,22}

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