Mechanical anisotropy at the nanoscale in amorphous solids
Yun Luo, Qi-Kai Li, and M. Li

Citation: Journal of Applied Physics 117, 044301 (2015); doi: 10.1063/1.4906408
View online: http://dx.doi.org/10.1063/1.4906408
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/117/4?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Deformation mechanisms, size effects, and strain hardening in nanoscale metallic multilayers under nanoindentation

Photopatterning the mechanical properties of polydimethylsiloxane films
J. Appl. Phys. 109, 054905 (2011); 10.1063/1.3552917

Spherical nanoindentation and deformation mechanisms in freestanding GaN films

Mechanical strength of nanocrystalline/amorphous Al 90 Fe 5 Gd 5 composites produced by rolling

Early stages of mechanical crystallization of amorphous FeZrBCu soft magnetic material
J. Appl. Phys. 87, 2464 (2000); 10.1063/1.372203
Mechanical anisotropy at the nanoscale in amorphous solids

Yun Luo,1 Qi-Kai Li,1 and M. Li1,2,a)
1School of Material Science and Engineering, Tsinghua University, Beijing 100084, China
2School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, USA

(Received 24 November 2014; accepted 10 January 2015; published online 22 January 2015)

Amorphous solids are randomly disordered without any long-range periodic atomic arrangement and thus appear isotropic. Here, we show in metallic glasses that this view does not hold at small scales: Strong mechanical anisotropy emerges when the sample size decreases below about 15 nm as shown by the marked deviation in stress-strain relations as well as elastic modulus along different loading directions. The size induced mechanical anisotropy is naturally related to structural anisotropy that is absent before loading. The anisotropic stress and modulus versus the size yield different scaling exponents in different stages of deformation, hinting at different deformation mechanisms. The size effect discovered here points to the existence of intrinsic heterogeneity defined by the anisotropy, which may play an important role in structure-property relations in amorphous solids. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4906408]

I. INTRODUCTION

Different from crystals, amorphous solids are disordered such that the constitutive atoms do not possess any long-range translational order. The random atomic structure has long been thought as the origin of the isotropic properties, that is, the properties are independent of direction in the material. In terms of mechanical response, for example, if an amorphous solid is subject to shear stresses in different directions, the induced shear strain would be the same along these directions and vice versa. This and other properties have been known for all types of amorphous solids from oxide glasses, covalent glasses to metallic glasses. Therefore, glassy materials are generally considered as isotropic. This view, built largely on continuum, is deeply rooted in our understanding such that we often extrapolate it to small scales. A typical example is the practice seen in ab initio calculations where samples with a few hundred atoms are routinely used in computing bulk properties.1–3 Another example is in constitutive theories and large scale atomistic modeling where the mechanical response of the amorphous materials is also considered directionally independent. In other words, isotropy is automatically assumed down to the smallest scales relevant to all mechanical responses.4,5 Therefore, in describing mechanical properties, any possible anisotropy, or heterogeneity, is removed. The same thinking prevails in practical application of amorphous materials in nanoscales where increasing number of applications have been explored recently.

In fact, there are several versions of anisotropy that have been known in amorphous solids. To distinguish them from the particular type of mechanical anisotropy to be reported here, we shall give a brief introduction here. The first is the initial structural anisotropy typically seen in thin metallic glass ribbons. It is found to lead to magnetic anisotropy.6 The structural anisotropy is caused by density gradient due to different cooling rates across the film thickness during rapid quenching. The second is the structural anisotropy from atomic clusters which are represented by preferred local atomic packing that is different from the random one perceived from macroscopic scales. The characteristic length scale of these clusters is typically a few atomic spacing.3 The third is the deformation induced mechanical anisotropy in both elastic and plastic regimes of metallic glasses.7,8 The induced elastic anisotropy is manifested in the change of the number of elastic constants and other nonlinear elastic responses.7,8 For example, the number of independent elastic constants increases from two when the samples are unloaded to five when under tension or compression; and the Zener anisotropic parameter could change by 50% at yielding.8 Experiment using energy dispersive x-ray and synchrotron scattering reveals that the deformation induced mechanical anisotropy is accompanied by induced structure anisotropy, that is, distance between the neighboring atoms along loading direction is different from other directions in the samples undergoing elastic, plastic deformation, or creep.9–15

These types of anisotropy in both structure and mechanical response are different from the nanoscale anisotropy to be introduced here in the following aspects: (1) The deformation induced mechanical anisotropy mentioned above is the same if the samples are deformed in different directions. That is, if shearing a glassy sample along different directions, we should obtain the same stress response. (2) For both structural and mechanical deformation induced anisotropies mentioned above, the relevant characteristic length is on the continuum scale. That is, one can measure them in samples with macroscopic scales. (3) In contrast, the length scales of the atomic clusters appear to be too small to be responsible for the continuum properties. In other words, their effect if exists at all would be easily averaged out over several atomic cluster spacing. Hence, the mechanical properties...
measured macroscopically can hardly be directly tied up to the anisotropy of the clusters. The vast difference in the length scales in these cases, therefore, does not help us in connecting the mechanical properties and the underlying microscopic mechanisms—something is missing on the nanoscale.

In this work, we show that deformation induced mechanical anisotropy persists in amorphous solids with reduced length scales down to tens of nanometers. The scenario is shown by the emergence of significant mechanical anisotropy in metallic glass samples with decreasing size. As mentioned above, the mechanical isotropy in amorphous solids is based on the assumption that the atomic packing is disordered and random, which goes down to the length scale at the first or second nearest atomic packing. In this work, we test this assumption by examining various samples with different sizes. We found that when the sample size decreases below about 15 nm, the samples begin to exhibit significant mechanical anisotropy which is manifested clearly in stress-strain relations and elastic modulus. This is done by deforming the small samples along different loading directions.

This new type of mechanical anisotropy is different from the abovementioned initial structure-induced anisotropy and deformation-induced elastic anisotropy in three aspects: (1) The magnitude of the length scale is far larger than the recognizable atomic structural heterogeneity defined by clusters, or the heterogeneity introduced by the nonaffine relaxation; (2) it is statistical in nature; and (3) it is different from that caused by thermal fluctuation. In the following, we shall detail our findings with an emphasis on these three characteristic features. Our result also suggests that amorphous solids are intrinsically heterogeneous defined by this length scale which should manifest in the mechanical properties of all topologically disordered solids.

This paper is organized as follows. In the next section, we shall go over the sample preparation and simulation methods used in this work. In particular, we use molecular statics simulation to model the deformation process where no thermal effect or temperature is present. Moreover, there is no explicit dynamics as there is no time involved. The purpose is to simplify our modeling and analyzing results. In Sec. III, we present the results obtained from the simulation. We first show the size dependent stress-strain relations, and the mechanical anisotropy. The anisotropy is defined as the deviation of stresses along different loading directions, which is different from the mechanical anisotropy described by the different elastic constants in continuum. The mechanical anisotropy leads to structural anisotropy in the small systems. We then show the scaling relations between the anisotropic mechanical properties and the sample size in different regimes of deformation. We also discuss the origins of the mechanical anisotropy arising from the small sample size. We propose a model based on the argument of “insufficient atomic packing space” for disordered atomic configurations. We also discuss the relations of the reported nanoscale anisotropy and those associated with clusters and nonaffine deformation. Finally, in Sec. IV, we summarize the results presented in this work.

II. METHODS

To carry out above tasks, we chose to use a binary metallic glass Cu64Zr36, primarily for its simplicity due to the non-directional interatomic bonding and lack of large structural units such as those in covalently bonded glasses. In the latter, one should naturally expect to see a larger intrinsic length scale in mechanical anisotropy defined by the large structure unit. Therefore, metallic glass offers a much stringent testing case for observing size induced anisotropy. This system has been used extensively in the past for investigation of glass formation, local ordering, mechanical properties, etc. The system parameters in the interatomic potential and sample preparation can be found in Ref. 26. Note that in general it is extremely challenging, if not impossible, to probe such small scale anisotropy experimentally in a systematic way due to the limited spatial resolution. This limitation makes the atomistic modeling a valuable option for now.

The liquid phase made of Cu64Zr36 is first prepared using Gibbs ensemble molecular dynamics (MD) simulation by melting a random crystalline Cu-Zr solid solution with fcc structure. The atoms in the system interact with periodic boundary conditions and are kept at zero pressure. The liquid is then equilibrated at 2000 K, a few hundred degrees above its melting point, for at least 250 ps and then cooled to 300 K with a cooling rate of 4 × 1011 K/s. The sample is subsequently relaxed at zero temperature so we can carry out molecular static simulation of shear. Therefore, we have a purely driven system without thermal effect and explicit dynamics. A number of samples with different sizes are prepared, ranging from 108 to 500 000 atoms, or about 1.2 nm to 20 nm in linear dimension.

To test the size dependent mechanical anisotropy, we performed simple shear along three different shear directions of the systems, that is, by applying three microscopic shear deformation strains $\gamma_{xy}$, $\gamma_{xz}$, and $\gamma_{yz}$ separately. The samples are deformed with the stepwise increment of shear strain $\Delta \gamma = 0.05\%$ per step. To accommodate the relaxation behavior of the sample during shear deformation, we allow the system to find the minimum energy configuration after each step by using a gradient descendent or energy minimization method. Thus, except the applied shear stress, there is no other stress left in the system. This condition is maintained at every applied deformation strain, so the system simulated remains in a well-characterized stress state of shear during the static deformation. Note that the shear is performed via deformation controlled process. That is, the system is deformed for a given external shear strain, which is fixed, and the corresponding shear stress is calculated when all other stresses and strains are relaxed. This point is relevant to the explanation to the “apparent residual stress” to be reported below.
III. RESULTS

A. Stress-strain relations and mechanical anisotropy in samples of different sizes

For an isotropic system undergoing shear deformation, the response, the shear stress along different shearing directions, would be the same within the range of certain statistic errors in experiment or simulation. Figure 1(a) shows the shear stress-strain relations for the metallic glass Cu$_{64}$Zr$_{36}$ composed of total 500 000 atoms, or about 20 nm in the cube edge length of the simulation box. The sample is sheared along $x$, $y$, and $z$ normal directions, or parallel to $yz$, $xz$, and $xy$ shear planes. Indeed, the three stress-strain curves overlap in the elastic region up to the maximum stress where plastic deformation sets in. The results indicate that the samples’ responses are similar in different directions, i.e., isotropic, up to the maximum stress. In plastic regime, the three stresses show some differences as marked by the slightly different maximum stress and zigzag shape with small amplitude. This is known to be related to initiation of local deformation that is random in nature.

From the stress-strain relation, we can obtain shear modulus $G = 34.7$ GPa (Figure 1(a)), which is close to the experimental result $G = 34$ GPa,$^{25,28}$ the yield stress $\gamma_Y = 1.24$ GPa, the maximum or peak shear stress $\gamma_{\text{max}} = 1.45$ GPa, and their corresponding strains $\gamma_Y = 3.78\%$ and $\gamma_{\text{max}} = 5.87\%$, respectively. These values are obtained by taking average over the corresponding results along different sharing directions. The yield stress is determined by using the 0.2% off-set strain rule, that is, by drawing a line parallel to the shear stress-strain curve near zero strain and with an interception on the strain axis at 0.2% strain. The interception of the line with the stress-strain curve gives the yield stress. These data set the reference for the isotropic system in our search for mechanical anisotropy in smaller samples.

Figure 1(b) shows three shear stress-strain relations for a smaller system composed of 4000 atoms, or about 4 nm in linear dimension. As seen clearly, the stress-strain curves are less smooth as compared with those in the larger system in Figure 1(a). There are abrupt rises and falls in the shear stresses which occur already near and above the yield point before the maximum stress is reached. Besides, the three shear stress-strain curves are not the same even in the elastic regime and the largest difference occurs at and beyond the yield point. Moreover, the shear modulus, the slope of the stress-strain curves, is different from that in the larger systems. Another obvious difference is that the rise and fall of the stress-strain curves in the plastic regime have larger amplitude and also larger intervals between each cycle of rise and fall as compared with those shown in Figure 1(a).

In addition, we observe finite stresses which show up immediately in the samples when small shear strains are applied, often at the first few steps in deformation strain increment. Since it occurs at small strains, the finite stress close to zero strain appears as “residual” stress; but it is certainly not in this case: a true residual stress is at zero applied stress. The reason for this unusual stress is because we hold fixed the external applied deformation strain, as mentioned above, the stress experienced by the small system cannot be released. As seen below, this phenomenon becomes more frequent and with larger magnitude as the sample size becomes smaller. When the system size becomes larger, such phenomenon disappears because in the large systems, local stress relaxation is easier and allowed, which also reflects the existence of the hidden length scale we are searching for in this work. Since the stress curves are shifted by the finite stress along different directions, the absolute shear stress-strain relations for the metallic glass Cu$_{64}$Zr$_{36}$ composed of total 500 000 atoms, or about 20 nm in the cube edge length of the simulation box. The sample is sheared along $x$, $y$, and $z$ normal directions, or parallel to $yz$, $xz$, and $xy$ shear planes. Indeed, the three stress-strain curves overlap in the elastic region up to the maximum stress where plastic deformation sets in. The results indicate that the samples’ responses are similar in different directions, i.e., isotropic, up to the maximum stress. In plastic regime, the three stresses show some differences as marked by the slightly different maximum stress and zigzag shape with small amplitude. This is known to be related to initiation of local deformation that is random in nature.

From the stress-strain relation, we can obtain shear modulus $G = 34.7$ GPa (Figure 1(a)), which is close to the experimental result $G = 34$ GPa,$^{25,28}$ the yield stress $\gamma_Y = 1.24$ GPa, the maximum or peak shear stress $\gamma_{\text{max}} = 1.45$ GPa, and their corresponding strains $\gamma_Y = 3.78\%$ and $\gamma_{\text{max}} = 5.87\%$, respectively. These values are obtained by taking average over the corresponding results along different sharing directions. The yield stress is determined by using the 0.2% off-set strain rule, that is, by drawing a line parallel to the shear stress-strain curve near zero strain and with an interception on the strain axis at 0.2% strain. The interception of the line with the stress-strain curve gives the yield stress. These data set the reference for the isotropic system in our search for mechanical anisotropy in smaller samples.

Figure 1(b) shows three shear stress-strain relations for a smaller system composed of 4000 atoms, or about 4 nm in linear dimension. As seen clearly, the stress-strain curves are less smooth as compared with those in the larger system in Figure 1(a). There are abrupt rises and falls in the shear stresses which occur already near and above the yield point before the maximum stress is reached. Besides, the three shear stress-strain curves are not the same even in the elastic regime and the largest difference occurs at and beyond the yield point. Moreover, the shear modulus, the slope of the stress-strain curves, is different from that in the larger systems. Another obvious difference is that the rise and fall of the stress-strain curves in the plastic regime have larger amplitude and also larger intervals between each cycle of rise and fall as compared with those shown in Figure 1(a).

In addition, we observe finite stresses which show up immediately in the samples when small shear strains are applied, often at the first few steps in deformation strain increment. Since it occurs at small strains, the finite stress close to zero strain appears as “residual” stress; but it is certainly not in this case: a true residual stress is at zero applied stress. The reason for this unusual stress is because we hold fixed the external applied deformation strain, as mentioned above, the stress experienced by the small system cannot be released. As seen below, this phenomenon becomes more frequent and with larger magnitude as the sample size becomes smaller. When the system size becomes larger, such phenomenon disappears because in the large systems, local stress relaxation is easier and allowed, which also reflects the existence of the hidden length scale we are searching for in this work. Since the stress curves are shifted by the finite stress along different directions, the absolute shear stress-strain relations for the metallic glass Cu$_{64}$Zr$_{36}$ composed of total 500 000 atoms, or about 20 nm in the cube edge length of the simulation box. The sample is sheared along $x$, $y$, and $z$ normal directions, or parallel to $yz$, $xz$, and $xy$ shear planes. Indeed, the three stress-strain curves overlap in the elastic region up to the maximum stress where plastic deformation sets in. The results indicate that the samples’ responses are similar in different directions, i.e., isotropic, up to the maximum stress. In plastic regime, the three stresses show some differences as marked by the slightly different maximum stress and zigzag shape with small amplitude. This is known to be related to initiation of local deformation that is random in nature.

From the stress-strain relation, we can obtain shear modulus $G = 34.7$ GPa (Figure 1(a)), which is close to the experimental result $G = 34$ GPa,$^{25,28}$ the yield stress $\gamma_Y = 1.24$ GPa, the maximum or peak shear stress $\gamma_{\text{max}} = 1.45$ GPa, and their corresponding strains $\gamma_Y = 3.78\%$ and $\gamma_{\text{max}} = 5.87\%$, respectively. These values are obtained by taking average over the corresponding results along different sharing directions. The yield stress is determined by using the 0.2% off-set strain rule, that is, by drawing a line parallel to the shear stress-strain curve near zero strain and with an interception on the strain axis at 0.2% strain. The interception of the line with the stress-strain curve gives the yield stress. These data set the reference for the isotropic system in our search for mechanical anisotropy in smaller samples.

Figure 1(b) shows three shear stress-strain relations for a smaller system composed of 4000 atoms, or about 4 nm in linear dimension. As seen clearly, the stress-strain curves are less smooth as compared with those in the larger system in Figure 1(a). There are abrupt rises and falls in the shear stresses which occur already near and above the yield point before the maximum stress is reached. Besides, the three shear stress-strain curves are not the same even in the elastic regime and the largest difference occurs at and beyond the yield point. Moreover, the shear modulus, the slope of the stress-strain curves, is different from that in the larger systems. Another obvious difference is that the rise and fall of the stress-strain curves in the plastic regime have larger amplitude and also larger intervals between each cycle of rise and fall as compared with those shown in Figure 1(a).

In addition, we observe finite stresses which show up immediately in the samples when small shear strains are applied, often at the first few steps in deformation strain increment. Since it occurs at small strains, the finite stress close to zero strain appears as “residual” stress; but it is certainly not in this case: a true residual stress is at zero applied stress. The reason for this unusual stress is because we hold fixed the external applied deformation strain, as mentioned above, the stress experienced by the small system cannot be released. As seen below, this phenomenon becomes more frequent and with larger magnitude as the sample size becomes smaller. When the system size becomes larger, such phenomenon disappears because in the large systems, local stress relaxation is easier and allowed, which also reflects the existence of the hidden length scale we are searching for in this work. Since the stress curves are shifted by the finite stress along different directions, the absolute
magnitude of the yield stress and the maximum stress measured from these systems is affected.

As we further reduce the sample size to 108 atoms with the cube edge length of about 1.2 nm, as shown in Figure 1(c), we observe the same jerkiness in the stress-strain curves as in Figures 1(a) and 1(b), but with much larger magnitude and longer interval between each cycle of stress rise and fall. Some of the samples show very large "residual" stress at the small, finite strain values. Some of these stresses even appear negative, meaning that they are in the opposite direction against the applied shear stress—since we subject the entire system to an applied shear strain with a positive sign which is done by increasing the shear strain and holding it fixed, the back stress can not actually bring the system back, which results in the negative stress. These internal stresses just reflect the complex stress state of the samples in the small systems.

Most importantly, from these stress-strain curves we can see clearly different responses along three different loading directions not only in plastic regime but also in elastic regime. This becomes more obvious as the sample size becomes smaller. As a result, the yield stress, maximum stress and their corresponding strain values, and shear modulus differ more from each other. We did not reduce the size further due to the concern that the cut-off distance in the interatomic potential begins to affect the result.

B. Structural anisotropy induced by deformation

The variation of the mechanical responses in different directions in fact represents another kind of mechanical anisotropy, albeit related to sample size. From the previous cases introduced, naturally one would ask whether or not the sample size induced mechanical anisotropy is originated from any pre-existing anisotropic structure. To confirm this, we checked the initial structures in different sized samples by using two dimensional radial distribution functions (2DRDFs) obtained from the atomic positions in the planes perpendicular to the shear plane. The 2DRDF is obtained from a plane, a thin layer with thickness of 2 Å. The 2DRDF is obtained using the relation,

\[ g(r, \theta) = \frac{n(r + \Delta r, \theta + \Delta \theta)}{a(r + \Delta r, \theta + \Delta \theta) \rho_0}, \]

where \( a(r + \Delta r, \theta + \Delta \theta) \) is the area of a plane bounded between the radial distance \( r \) and \( r + \Delta r \) in the plane, and polar angle \( \theta \) and \( \theta + \Delta \theta \); \( n(r + \Delta r, \theta + \Delta \theta) \) is the number of atoms inside the area, and \( \rho_0 \) is the mean number density in two dimensions. We obtain three 2DRDFs in the planes with each perpendicular to a different shear direction. A series of the 2DRDFs from different layers in each direction are taken and used in obtain the average.

Using the 2DRDF is for the following reasons. First, structural anisotropy, if exists at all, is small in either the initial structure or induced one by deformation. Second, it is directional, especially if it is induced by deformation. The 2DRDF from the planes perpendicular to the shearing direction can effectively capture the subtle change. As a comparison, the RDF in 3D is obtained by averaging atomic positions in all directions and thus masks the subtle structural anisotropy, which is orientation sensitive and also small in value. For an isotropic material, the 2DRDF is a perfect circular ring in all directions, and it becomes distorted from the circular rings, usually into an ellipse in anisotropic case. The Fourier transform of the real space 2DRDF is directly related to the 2D structural factor obtained, for example, from synchrotron experiment. For simple shear, the ring is expected to distort along the 45° angle with respect to the shear direction, the maximum shear stress direction.

Figure 2(a) is the 2DRDF in three shear directions in unloaded samples before shearing. The perfect circular rings show no sign of initial structural anisotropy in all samples of different sizes, which indicates that the mechanical anisotropy does not have a structural origin, even down to about 1 nm. However, deformation leads to structural anisotropy. As shown in Figure 2(b), under shear the circular ring in isotropic samples changes to ellipse in the 2DRDF along the 45° angle away from the shear direction. The degree of induced structural anisotropy can be gauged by the degree of distortion in the 2DRDF rings. We obtained three 2DRDFs from samples at three representative macroscopic shear strains, 1.5%, 5%, and 15%. The structural anisotropy as shown by the distorted rings increases from the elastic regime at 1.5% strain and reaches the maximum at the maximum stress at 5% yield strain before decreasing in the plastic regime at 15% strain. In plastic regime, the structural anisotropy eases up considerably (Figure 2(b)). The observation is corroborated by other measurements shown below.

C. Size dependence of mechanical anisotropy

Next, we give a quantitative description of the above observations of the size induced mechanical anisotropy. The mechanical anisotropy here is expressed by the standard deviation (SD) from the mean of the stresses in the stress-strain curves along three different shearing directions. Thus, the bigger the SD is, the larger the mechanical anisotropy. The mechanical anisotropy is shown to depend strongly on sample size. In addition, we found the variation of the mechanical anisotropy at different deformation strains. To monitor the dependence of the SD on deformation strain, we picked four characteristic macroscopic shear strain values subject to the system at 1.5, 3, 5, and 15% which correspond to four typical regimes in deformation, respectively: elastic, close to yielding, maximum stress, and plastic deformation.

Figure 3(a) shows the values of the relative standard deviations (RSDs) versus the system size measured by the sample side length at the corresponding macroscopic strains. The RSDs of the shear stresses from the mean along three independent shear directions at the corresponding shear strains are taken over 18 samples prepared independently. The results show first that the mechanical anisotropy is the largest for all systems in the elastic regime and becomes smaller in the plastic regime, which agrees with the trends of structural anisotropy shown by the 2DRDFs in Figure 2(b). We enlarge the results for the small systems in the inset in Figure 3(a) to emphasize the change there.
Second, the mechanical anisotropy increases monotonically with decreasing sample size. For the smallest system we tested, $N = 10^8$ atoms, the anisotropy is the largest at all four strains as shown by the RSD reaching roughly about 200% at yielding and 100% in plastic regime. As the sample size increases, the RSD decreases. At about 15 nm in linear sample dimension, the RSD already reach to less than 5%, which is comparable to the upper bound of the statistical errors in the simulation. As the sample size increases further, the deviation decreases further, which can be seen more clearly in Fig. 3(a). And when $N = 500,000$ atoms or about 20 nm in the linear dimension of the sample, the RSD drops below 0.5%. At this and larger sample size, we did not see any mechanical anisotropy, which is consistent with the results shown in Figure 1(a).

The mechanical anisotropy is also reflected in the elastic shear modulus, the slope change of the stress-strain relation. Fig. 3(b) shows the relative values of the RSDs for the shear modulus versus different sample size obtained from the stress-strain curves. The RSD of the modulus also shows the monotonic decreasing trend versus sample size. The deviation subsides from over 20% to less than 1% when the sample size goes above 10 nm which is within the accepted range of error in experimentally measured modulus.29

As a side note, we like to mention in passing that the variation of elastic shear modulus is considered as an effective measure for elastic heterogeneity of amorphous solids.27,30,31 It is usually obtained by using the so-called fluctuation formula in molecular dynamics simulations.27,30,31 But the convergence of the calculation is often not desirable. Our results suggest that the approach using stress-strain curve appear to be more efficient—only tens of thousands steps are needed versus millions in obtaining reliable elastic constant in amorphous solids.

D. Size scaling relation of variations in stress and modulus

So far, we have shown two key results, the large deviation in mechanical responses in different loading directions and the statistical nature of the mechanical anisotropy in the ever smaller samples. The mechanical anisotropy is measured via the standard variation of the stress and modulus along different shear directions. We also show that the anisotropy, either mechanical or structural, is different at different external shear strains. These results bring up a relevant question about deformation in amorphous solids in general: Are the observed mechanical anisotropy, represented as the variance of various mechanical properties, simply caused by thermal fluctuation? Or conversely, does the deformation induced variation of mechanical properties resemble that of thermal fluctuation?

It is known that in the small elastic strain limit, i.e., small strain limit, thermal fluctuation in equilibrium system at finite temperature leads to scaling relation between the RSD of the mechanical properties such as stress, strain and elastic modulus and the sample size, $1/N^x$, with $x = 0.5$ and $N$ the number of atoms. For a driven system at zero temperature such as the sheared metallic glass in this work,
thermal fluctuation is clearly absent. So, would the RSDs still obey the same scaling relation, especially at the finite deformation strains in different deformation regimes?

Our results indicate that one may not make a straightforward analogy, even at small strain limit. One reason is the strong directional effect of the tensorial quantities of stress and strain in amorphous systems under shear, such as the quadrupolar stress; the second is the anisotropy and heterogeneity in the mechanical properties in the disordered system as we observed here; the third is the presence of finite stress in the system at small deformation; and the last is the different anisotropic responses shown in different deformation regimes. Collectively, they may give rise to different results.

To see how these expected effects manifest, we performed numerical fitting of the stresses and shear modulus versus sample size with a power law relation,

$$\frac{N}{C_0}^a \text{ or } \frac{L}{C_0}^b,$$

where $N$ is the number of atoms in the system, $L$ is its linear dimension, and $a$ and $b$ are free coefficients to be determined. For homogeneous system in three dimensions, $N \propto L^3$ and $\beta = 3\alpha$. Using the RSD data of the stresses in Figure 3(a), we obtained $\alpha = 0.540 \pm 0.026, 0.567 \pm 0.025, 0.548 \pm 0.034,$ and $0.495 \pm 0.018$ at the four macroscopic strain values of 1.5, 3, 5, and 15%, respectively. The exponent differs not only in different regimes of deformation but also from that of the homogeneous equilibrium at the small elastic strain limit. The change of the exponent shows that the system differs more from the thermal equilibrium as the deformation strain increases till the maximum stress is reached; and in plastic regime it becomes more like in thermal equilibrium, which is consistent with the observed structural anisotropy change shown in Figure 2(b).

The same fitting procedure for the RSD of the shear modulus, which is done at zero strain limits, gives an exponent of $0.572 \pm 0.035$ (Fig. 4(b)). It is different from that caused by thermal fluctuation in the equilibrium systems.$^{32}$ Note that in our case, the samples are deliberately kept at zero temperature to eliminate thermal effect. At larger strains, the variation of the shear modulus cannot be obtained simply from the stress-strain curves due to the nonlinear elastic effect.$^{34}$ This prevents us from observing the trend in the change of the scaling exponent in shear modulus at different strains. However, from the results of the stresses, we

FIG. 3. (a) The relative standard deviation of the stresses versus the sample size measured by the side length of the simulation box. They are selected at 1.5, 3, 5, and 15% macroscopic deformation strains, respectively. The symbols are the relative standard deviation of the stresses at the macroscopic shear strain and the lines are from the best fitted power law relation for these data. The inset is the zoom-in plot of the stress variation in small sample size where the stress variation differs from each other the most. (b) The relative standard deviation of the shear modulus versus the sample size. The inset is the absolute values of the modulus. The symbols are the data from the simulation and the lines from the power law fitting.

The same fitting for the RSD of the shear modulus, which is done at zero strain limits, gives an exponent of $0.572 \pm 0.035$ (Fig. 4(b)). It is different from that caused by thermal fluctuation in the equilibrium systems.$^{32}$

FIG. 4. (a) The scaling relation between the relative standard deviations of the stresses versus the sample size in log-log plot. The exponent is obtained from each of the curves at different deformation strains. The symbols are the relative standard deviation of the stresses at the macroscopic shear strain and the lines are from the best fitted power law relation for these data. (b) The scaling relation between the relative standard deviations of the shear modulus versus the sample size in log-log plot. The symbols are the relative standard deviation of the stresses at the macroscopic shear strain and the lines are from the best fitted power law relation for these data.
could reasonably expect to see the same trend at larger deformation strains.

**E. Effect of metastability**

As seen early, there are several unusual results in the stress-strain relations in small systems, one of which is the residual-like stress shown up at small deformation strains. They contribute to the anisotropy, especially the RSD in stresses. The appearance of these stresses at the small deformation strain may have different origins, one of which is related to the structural metastability typically occurring in glassy systems. To check this, we performed additional “mechanical” relaxation by load and unload slightly the system which exhibits the finite stresses, in hope that the agitation of the shear stress can loosen up some of the metastable configurations. Our result shows, however, such exercise does not lead to significant reduction of the finite stress (Fig. 1(c)).

To further check if the size induced mechanical anisotropy is a genuine response of the small sample to external stimulus, or due to other reasons, we also looked at how equilibration during sample preparation could lead to configuration changes, especially the unstable or metastable ones that may be mistaken as the source for the mechanical anisotropy. Insufficient equilibration time in liquid state, for example, could lead to inhomogeneous atomic configurations inherited from either the initial structure or metastable ones. To this end, we performed additional equilibration by holding the samples in liquid state for different time in hope to erase any possible metastable configurations possibly left in the solids quenched from the liquid. The holding time ranges from tens to hundred nanoseconds. Our result shows no significant difference in the final results. Some of these results have been shown in Figure 3 where multiple data points are shown at each given sample size.

**F. Origin of the size dependent mechanical anisotropy**

In crystalline materials, stress-strain curves also show jerkiness, which is known to be caused by defect nucleation and propagation when sample size is small.\(^\text{35}\) But the response remains the same in different shearing directions along the same crystallographic orientation, at least in elastic regime. Amorphous solids do not have extended structural defects such as dislocations or grain boundaries and also no pre-existing structural anisotropy. Therefore, there seems no structural basis to cause large deviation of the mechanical responses in different loading directions. The size induced mechanical anisotropy in amorphous solids must, therefore, arise from different origins.

The first connection one may immediately bring up is the shear transformation zone or non-affine deformation that indeed shows local deformation regions different from the macroscopic strain.\(^\text{16-21}\) However, the scales of these local deformation zones are small, ranging from a few atomic spacing to a few nanometers. We argue here that they, therefore, should not be considered as the cause; rather they may likely be the result. The underlying cause, especially the structural origin, is yet to be identified.

By zooming into smaller sample size as done in our simulation and examining the mechanical response, we saw very large local deformation with statistical nature that does not resemble thermal fluctuation. From these results, we can reasonably attribute the origin to a simpler reason, the *insufficient atomic packing space*. The argument goes as follows: If the system size is large enough, the system could allow for realization of many different atomic packing configurations, such that a truly random and homogeneous distribution of atoms can be achieved. Otherwise, only limited realization or configuration of atomic packing can be achieved in small samples. This can be explained with a simple example below. Suppose we put certain number of balls randomly in a box. If the box is small (with respect to the size of the balls), one can only realize a finite number of allowed packing configurations in arranging the balls in the box, although the packing itself is done randomly. The finite number of realizations of the “random” atomic configurations confined by the small space leads to “bias,” not only in atomic packing but also in atomic interactions among the atoms in the finite volume. Together they manifest as mechanical anisotropy when the system is agitated by external mechanical force. This type of mechanical anisotropy is statistical in nature—if the sample is sufficiently large, the variances from the size limit can cancel each other, leading to both structural and mechanical isotropy as observed in Figure 1(a) and in experiment where sample size is often large enough to reach continuum limit, which leads to the scaling relation in thermal fluctuations.\(^\text{32}\)

This reasoning can also be demonstrated more explicitly by “combining” many small, standalone systems generated in this work. Since each small system differs from others randomly, their responses are different and statistical in nature. However, if a large number of such small systems are taken to obtain the average of the mechanical properties, the isotropic behavior could be recovered. Figure 5 shows the stress variation versus the sample size in such a “composite” system made of many independent systems containing 500 atoms each. The means and variances are obtained from the number of the small systems in the composite. As we adding more and more small samples into the average, the total number of atoms as well as the equivalent sample size becomes bigger. And indeed, the variance of the shear stresses decreases with the size in the composite system. Note that although we can illustrate the concept, the composite made of independent small systems gives us quantitatively different size effect. For example, the scaling exponents are different (the inset in Figure 5). From the data in Figure 5, we obtained \(z = 0.739(\pm 0.038)\), \(0.601(\pm 0.043)\), \(0.577(\pm 0.024)\), and \(0.605(\pm 0.020)\), respectively, at the macroscopic strain values of 1.5, 3, 5, and 15%, respectively. The values are larger than those from the standalone systems (Figure 4(a)). Moreover, the fluctuation in elastic regime exhibits a monotonic trend as indicated by the decreasing exponents with increasing strain.

From this simple model, nevertheless, we can predict two consequences in mechanical deformation of amorphous solids. One is *statistical nature* and the other is *localization or spatial heterogeneity*. Different from crystal anisotropy,
size induced anisotropy in amorphous solids is random and therefore does not survive in sufficiently large samples. That is, their properties are different and vary within certain characteristic length scales. The spatial heterogeneity may likely be the cause that initiates localization in mechanical responses, stress, strain, and modulus, etc.

However, we must recognize that the measurement of the characteristic length depends on the quantities used in the measurement; The length scale measured from the anisotropic mechanical response, both elastic and plastic, gives a length scale of about 15 nm in the metallic glass; whereas if we consider the atomic clusters in the initial isotropic structure or shear transformation zone, the length scale goes down to the nearest neighbor atom separations. Early work from measuring non-affine displacement field shows about 3 to 5 nm length scale. Comparing these different length scales, we suggest that the length scale identified from the size induced mechanical anisotropy is perhaps more meaningful from the practical consideration, as mechanical properties are the most relevant quantity in measuring mechanical response. Incidentally, this length scale coincides remarkably well with the minimum size of shear bands found in metallic glasses in both experiment and computer simulation, although the underlying connection still needs to be established.

IV. SUMMARY

We have observed the sample size induced mechanical anisotropy in an initially homogenous binary metallic glass. We attributed the cause to the insufficient statistical realization of different random atomic configurations in limited space or volume. Therefore, the mechanical anisotropy is statistical in nature and size dependent, and should be different from the usual thermal fluctuation. This finding points to the existence of a structural basis of the size about 10–15 nm below which strong mechanical anisotropy shows up. Thus, the concept of isotropy and homogeneity in glasses only makes sense when defined in a statistical sense in large systems and if a sufficiently large number of these motifs are assembled. In other words, the mechanical response of a metallic glass should be considered as anisotropic on the length scale close to the critical length scale, about 15 nm in our case.

This conclusion may resurrect the old idea of glass, the “quasi-crystalline” model in which a glass is considered as composed of small patches of small size crystals, or “microcrystal” as it is called. This proposal was originated from consideration of electronic transport properties of glassy materials, although the existence of such local anisotropy was unknown at the time. Subsequent research has not found any microcrystal either. Our work shows that there is no need for the existence of microcrystals—amorphous packing itself is capable of generating significant anisotropy at small scales in both property and structure which resemble that of micro crystals.

But in dealing mechanical properties of disordered materials, local anisotropy or mechanical heterogeneity has seldom been considered in both atomistic and continuum models. Obviously, the next natural extension of this work is to explore how the mechanical heterogeneity manifests in overall mechanical properties of disordered materials such as constitutive relations in continuum. We hope that this work would contribute to establishment of new constitutive models that can take this intrinsic property into proper account.

ACKNOWLEDGMENTS

We acknowledge the financial support for this work provided by the National Thousand Talents Program of China. M.L. also like to thank the support provided by the National Science Foundation (NSF) under the Contract No. NSF-0907320.