Deformation of metallic glasses: Recent developments in theory, simulations, and experiments.

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Abstract

We review recent research into elastic and plastic deformation of metallic glasses, with an emphasis on making connections between developments in theory and simulation (largely from the physics community) and experimental results (largely from the metallurgy community). Topics covered include strain measurement via scattering techniques, non-affine atomic displacements during elastic deformation, shear transformations, constitutive equations, shear bands, and strain hardening. Where possible we connect the observed behavior and properties to the structure of the glass on the atomic- and nano- scales.

Keywords: Metallic glass, amorphous alloy, disordered material, elastic deformation, plastic deformation.

1. Introduction

Over the more than fifty years since their discovery [1] there has been extensive research into the structure and properties of metallic glasses. The earliest metallic glasses required rapid solidification and could therefore be produced only in limited forms. The development of bulk glass-forming alloys [2–4] not only provided samples suitable for traditional mechanical testing techniques but

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also raised the possibility that amorphous alloys might be employed in structural applications.

In 2007, two of us were co-authors on a review article summarizing the state of understanding of mechanical behavior of metallic glasses and proposing directions for future research [5]. Since then interest in the mechanical behavior of metallic glasses has remained intense and an updated review seems timely. In this article we review several areas where significant progress has been made and develop a few new ideas, particularly with regard to insights from theoretical and computational investigations of mechanical response of amorphous alloys (and disordered materials more generally). For a more comprehensive discussion we refer the reader to the earlier review [5] or to several other reviews of mechanical behavior of metallic glasses that have been published since 2007 [6–11].

The central paradigm of materials science states that the structure, properties, and processing of materials are interrelated. The periodicity of crystalline materials facilitates connections between their mechanical response and their atomic-scale structure, both experimentally (for example, by making dislocations visible in transmission electron microscopy) and theoretically. Such connections are much more challenging in metallic glasses, which lack long-range order and therefore are not as amenable to detailed characterization by traditional diffraction-based techniques. Nevertheless, experimental investigations using nanoscale probes now complement a rich set of computer simulations and theoretical analyses [12, 13] to provide an emerging consensus of the phenomenology of the structural origin of mechanical response in these materials.

Connections between structure and properties, therefore, provide a unifying theme for the topics discussed in this review. After a brief review of our current understanding of the structure of metallic glasses, we begin our discussion of mechanical behavior at the atomic- and nano-scale by considering the use of scattering techniques for measuring elastic strain in metallic glasses, and the implications and limitations of this new technique. This leads into a discussion of non-affine atomic displacements during elastic deformation and the connection of these features to plastic deformation through shear transformations. We next

consider how the structure of metallic glasses evolves under load and recent attempts to capture this evolution in the form of constitutive relations that could be useful for modeling of mechanical behavior. Moving to larger length scales, we examine localized plastic flow in shear bands with an emphasis on recent studies of their structure and dynamics. This introduces the topic of strain hardening in metallic glasses, through two recently-reported mechanisms: Exhaustion hardening and inherent hardening by relaxation. As in our original review [5], the last section points out important and promising directions for future research.

2. Structure of metallic glasses

The salient feature of the structure of metallic glasses is that they are disordered—a statement that is not as much of a truism as it may appear. The possible structural states of matter occupy a continuum from the perfect regularity and homogeneity of defect-free crystals to the utter disorder of ideal gases. Liquids and glasses are undoubtedly among the more disordered forms of condensed matter, but exactly how much structural order exists, what form it takes, and the length scale over which it extends are difficult questions that are the subject of ongoing research. The literature on this subject is extensive, but fortunately a comprehensive review of the structure of metallic glasses has recently been provided by Cheng and Ma [8], along with a more recent brief review by Ma [14]. In this section we highlight several key results that are important for understanding what follows; the interested reader is referred to those papers for a more complete discussion.

To begin at the shortest length scales, the high density and non-directional bonding of metallic glasses imply a high degree of short-range order based on close-packing of atoms. The basic packing unit is a tetrahedral cluster of four atoms; by allowing each atom to participate in several such clusters it is possible to achieve a high packing density, but because it is impossible to fill space with tetrahedra some degree of geometrical frustration is required (Fig. 1). Different

Figure 1: Space-filling packing of regular tetrahedra is not possible, as illustrated here for the case of five tetrahedra sharing a common edge. (Figure based on an original in Ref. [16].)

glasses have different structural motifs, or preferred ways of packing tetrahedra (and accommodating the inevitable geometrical frustration). Chen and Ma refer to these different tetrahedral packings as “Z clusters” [8, 14] (Fig. 2).

One much-discussed Z cluster consists of twelve atoms arranged at the vertices of an icosahedron around a central atom; in such a cluster the central atom plus any three mutually adjacent surface atoms form a tetrahedron (usually distorted). Although “five-fold” bonds—clusters where two adjacent atoms have five neighbors in common—are frequently observed, they should not be taken as indicative of icosahedral clustering which is, in fact, not very common. Rather, the presence of the five-fold bonds reflects dense polytetrahedral packing with a minimum of rotational defects [14, 15].

An example of the connection of atomic-scale structure to mechanical behavior is provided by atomistic simulations of Cu-Zr alloys. The fraction of Cu-centered icosahedral clusters increases dramatically as the liquid is cooled towards the glass transition, which is correlated with slowing dynamics of the system [15, 18, 19]. Adding Al to this simulated alloy enhances the development of icosahedral clusters, further slowing the dynamics [20]. The influence of short-range order extends to the glassy state where locally greater icosahedral order correlates with higher stiffness and resistance to yield. Regions of the

Figure 2: (a) Atomic configuration of a $\text{Cu}_{64}\text{Zr}_{36}$ metallic glass from molecular dynamics simulation [17] with 128,000 atoms and a box size of 12.74 nm. Gold spheres represent Zr atoms and grey, Cu. (b) Representative atomic clusters centered on Cu and Zr. The preferred cluster around copper is a full icosahedron with 12 nearest neighbors (Z12) while the larger Zr atoms can accommodate clusters with 16 near-neighbors (Z16). (c) A supercluster of 79 atoms, with eight interconnected Cu-centered full icosahedra indicated by dashed circles. Clusters can interconnect by sharing vertices, edges, or faces, or they can be interpenetrating. (d) Network of interconnected icosahedra indicated by line segments connecting the Cu atoms at the center of each cluster. (Images provided by Jun Ding and En Ma.)

structure without this favorable short-range order, which have been called “geometrically unfavorable motifs” (GUMs) [14], have lower stiffness and a greater tendency to undergo shear transformations [21, 22] as will be discussed in more detail below.

This last observation points out the importance of structural heterogeneity for understanding mechanical behavior of metallic glasses. It is reasonable to suspect that this heterogeneity may reflect the structure of the supercooled liquid from which the glass forms. Because of intense interest in the fundamental nature of the glass transition itself, the structure and dynamics of supercooled liquids near the glass transition have been the subject of extensive research [23] and there is strong evidence of increasing inhomogeneity upon cooling towards the glass transition [24, 25].

Beyond the nearest-neighbor interactions some kind of so-called “medium-range” order is required to achieve the high densities observed for metallic glasses. The most developed theory of medium-range order in metallic glasses is the efficient cluster packing model of Miracle and coworkers [26, 27]. This model begins with short-range order clusters similar to those discussed above (but centered on solute atoms) and then posits that these clusters are themselves arranged to produce efficient overall packing, for instance into fcc arrays. The structural order is presumed to extend over only a few cluster diameters. The densities predicted on the basis of this model are in reasonable agreement with experiment, and the model has some success in reproducing experimental measurements of the separations of solute atom pairs [27]. As with the nearest-neighbor interactions, it is reasonable to suppose that the structure is heterogeneous on these larger length scales.

3. Elastic deformation

To a metallurgist, elastic deformation of crystals is among the simplest mechanical behaviors to understand. At small strains ($< 0.2\%$) deformation is fully reversible and follows Hooke’s law (although non-linear and anelastic behavior

can also be observed if the crystal has impurities or defects, or at large strains). At low temperatures in simple crystals this elastic response can be calculated as the stress resulting from fully affine deformation of the lattice—that is, a simple rescaling of the lattice parameters commensurate with the imposed loading conditions, accomplished by simply stretching (or compressing) primary atomic bonds.

It has become apparent over the last few years, however, that elastic deformation of metallic glasses is considerably more complex. Unlike crystals, in a disordered material every atom has a unique atomic environment and so the response of every atom to the macroscopic loading conditions can, in principle, be different. This difference leads to a variety of effects, including non-linear behavior, anelasticity, microplasticity at very small strains, and elastic behavior that apparently depends on the length scale of the measurement.

3.1. Measurement of elastic strain with scattering techniques

The use of diffraction techniques to measure elastic strains in crystalline materials has a well-founded physical basis in the direct relationship between the positions of diffraction peaks and the corresponding interplanar spacings expressed in Bragg’s Law [28]. Poulsen and coworkers were the first to report that analogous measurements are possible for a metallic glass [29], although it is interesting to note that similar experiments were performed on amorphous polymers more than thirty years ago [30]. Reference [31] provides a review of this topic; here we highlight some important considerations and recent results.

One way to measure elastic strains in an amorphous material using scattering data is to measure changes in position of the maximum in the scattered intensity $I(q)$ directly (where q is the magnitude of the scattering vector). For measurements of elastic strain the assumption is that the position of the maximum is inversely proportional to some average atomic spacing in the material so that the strain can be calculated from

$$\epsilon = \frac{d_\sigma - d_o}{d_o} = \frac{q_o}{q_\sigma} - 1, \quad (1)$$

Figure 3: Elastic strain in a metallic glass can be measured from the distortion of the rings of scattered radiation. (a) Schematic of an asymmetric four-point bend specimen (left). Under load a state of nominally pure shear stress σ is produced in the test region, which is equivalent to tensile and compressive normal stresses of the same magnitude in a coordinate system rotated by 45° to the original (right). (b) Corresponding scattering measurements from a Zr-based metallic glass. In the strain-free state (left) the scattering rings are circular. Loading to near the nominal yield stress in shear (center) distorts the rings into ellipses. The distortion is too small to see at this scale, but is clearly shown by taking the difference of the loaded and unloaded scattering patterns (right).

where d_o and q_o are the average interatomic spacing and peak position in the strain-free state, and d_σ and q_σ are the corresponding values under a macroscopic stress σ . To keep our notation simple we have written ϵ as a scalar although in reality it is a component of the strain tensor, and the values of d_σ and q_σ depend on the loading condition (Fig. 3) [32].

Although Eqn. 1 has been widely used, some caution is necessary. Implicit in the treatment leading to Eqn. 1 is the assumption that the structure of the material is not strongly perturbed by the strain state [33]. This is probably a reasonable assumption for small elastic strains (although as noted in Sec. 4 below there is growing evidence of irreversible atomic rearrangements even well below the macroscopic yield stress) but may not hold at stresses approaching the yield

stress [34] and certainly does not hold if the structure is significantly altered
 155 for, example, by plastic deformation [35] or ion irradiation [36]. Whether or not
 simple structural relaxation by annealing near the glass transition temperature
 is sufficient to invalidate Eqn. 1 is an open question, although we note that
 attempts to measure volumetric thermal expansion near T_g appear to produce
 reasonable results [37]. The basic requirements are to ensure that there is a valid,
 160 strain-free structural state as a reference and that the loading or processing
 history of the specimen does not alter the structure to such a degree as to
 invalidate the assumptions inherent in Eqn. 1.

Much of the early work focused on uniaxial tension or compression tests to
 establish that scattering-based strain measurements produced results consistent
 165 with other techniques. For example, in a uniaxial test the stress is known
 and the elastic strain can be measured according to Eqn. 1 as a function of
 orientation with respect to the loading direction, from which Young's modulus
 E and Poisson's ratio ν can be determined, under the assumption that the
 material is elastically isotropic. The agreement between the elastic constants
 170 determined in this way and those obtained from other techniques (ultrasound or
 measurement of strain via extensometer or strain gage in quasi-static testing)
 is reasonable but there are apparently systematic differences (Fig. 4). The
 reasons for these discrepancies are not clear, but they are an indication that the
 x-ray strain measurements are not measuring precisely the same thing as more
 175 traditional techniques.

If the strain state can be accurately measured with a scattering technique,
 then interesting possibilities ensue. For example, one can measure the local
 strain in specific regions of a sample under complex loading. Fig. 5(a) shows
 the von Mises effective stress around a mode I crack tip in a metallic glass.
 180 Part (b) of the figure shows that the stress falls off as the inverse square root of
 the distance from the crack tip, as predicted by linear elastic fracture mechanics.
 Near the crack tip this relationship does not hold because the x-ray strain-stress
 relationship becomes nonlinear, as mentioned above.

Figure 4: Agreement of (a) Young's modulus and (b) Poisson's ratio between x-ray strain measurements and measurements from other techniques (ultrasound, extensometer, or strain gauge). Data from references [33, 34, 38–45].

Figure 5: (a) Crack-opening normal stress (σ_{xx}) around a mode I crack in a single-edge notch bend specimen of a Zr-based metallic glass at a stress intensity of $K_I = 47 \text{ MPa m}^{1/2}$ measured with high-energy x-ray scattering, compared to a linear elastic calculation. (b) σ_{xx} as a function of distance ahead of the crack tip (r) at $K_I = 76 \text{ MPa m}^{1/2}$. Far from the crack tip σ_{xx} falls off as $r^{-1/2}$ as predicted by fracture mechanics. The deviation from $r^{-1/2}$ behavior close to the crack tip is due to plasticity and non-linearity of the x-ray strain measurement. From Ref. [32] and used under the terms of the Creative Commons Attribution License.

3.2. The influence of non-affine atomic displacements on elastic response

A second way to extract strain information from scattering data is to normalize the scattered intensities $I(q)$ to produce the total structure factor $S(q)$, and Fourier transform $S(q)$ to get the pair distribution function, $\rho(r)$. The peaks in $\rho(r)$ correspond to the distances of atomic coordination shells around an average atom in the material, so shifts in these peak positions due to mechanical loading can be interpreted as elastic strains [29, 33]. (Note that if the loading condition introduces a significant structural anisotropy then this must be taken into account by expanding both $S(q)$ and $\rho(r)$ in terms of spherical harmonics; see Refs. [46, 47] for a discussion.)

An interesting result of this procedure is that the strain calculated from shifts in the $\rho(r)$ peak positions depends on which peak is used, with the strain being smallest for the atomic first near-neighbors and asymptotically approaching the macroscopically imposed strain [29, 33, 47]. This apparent length-scale dependence of strain is not entirely understood. Poulsen and coworkers attributed it to unspecified atomic rearrangements on length scales of ~ 0.5 nm [29]. More recent molecular dynamics simulations by Vempati and coworkers show that the apparent length-scale dependence of strain from $g(r)$ is smaller under hydrostatic loading than under uniaxial loading [47]. Because hydrostatic loading lacks a macroscopic component of shear strain, this finding suggests that the length-scale dependence of strain is associated with non-affine atomic displacements, which are promoted by shear strains. Vempati and coworkers pointed out that non-affine atomic displacements can result in a change of atomic nearest neighbors around a given atom, and since $g(r)$ is effectively a histogram of near-neighbor distances, changes of this kind in the local environment may partially explain the apparent length-scale dependence of strain; other algorithms for calculating strain from the atomic configurations show different length-scale dependencies, or none at all [47].

These non-affine atomic displacements affect the mechanical response of metallic glasses. For example, it has long been recognized that metallic glasses are more compliant (less stiff) than crystals of similar composition (Fig. 6) [48,

49]. The additional compliance is inherent to all non-crystalline solids and is a reflection of the disordered structure [50–52]. In a homogeneous structure, a homogeneous strain necessarily results in a homogeneous stress and the elastic constants can be derived in terms of derivatives of the atomic potential energy with respect to strain; the result is commonly called the Born contribution to the elastic constants. (This statement is strictly true only at zero temperature because it ignores entropic contributions which may become important at finite temperatures.) In an inhomogeneous structure, on the other hand, a homogeneous strain results in an inhomogeneous stress and non-affine displacements of the atoms can reduce the internal energy of the solid. This results in a negative contribution to the elastic modulus, reducing it relative to the Born contribution alone [50]. The heterogeneity of non-affine displacements is a reflection of the fundamentally heterogeneous structure of amorphous solids and has been explored in simulations of a variety of systems, including metallic glasses [15, 53], two- and three-dimensional Lennard-Jones glasses [54, 55], silica [56], amorphous polymers [52], and granular materials [57]. Typically these simulations show deviations from Hooke’s Law on short length scales (the particular length scale depending on the system being studied) and a strong heterogeneity of elastic response on intermediate length scales. Only at longer length scales does the response become homogeneous and linear.

An important direction for research is to move from these general considerations towards an improved understanding of the relationship between specific aspects of the structure and the resulting mechanical response. For example, a strong contribution of non-affine relaxation to the elastic response is apparent in three-dimensional simulations of $\text{Cu}_{64}\text{Zr}_{36}$, in which it has been further observed that the non-affine contribution to the elastic response varies dramatically with the preparation of the glass, particularly the rate of quenching [15]. This particular glass exhibits a high degree of icosahedral short-range order, and regions of high modulus correlate with icosahedrally coordinated Cu-centered clusters.

Figure 6: (a) The bulk modulus (K) of a metallic glass is typically some 5–10% lower than that of a crystal of the same composition, but the shear modulus (b) is 20–30% lower. Data from Ref. [9]

245 3.3. Mechanical instabilities and the potential energy landscape

2 The disordered, heterogeneous structure of metallic glasses suggests that
 3 we should expect a complex variety of atomic rearrangements in response to
 4 externally-imposed displacements. Some of the non-affine rearrangements de-
 5 scribed above, which occur at small strains, are clearly non-dissipative—they
 6 are fully reversible without the dissipation of energy as heat. In these rearrange-
 7 ments atoms of different types continuously adjust to their local environments as
 8 the material is subjected to remote strain. As the strain increases, however, it is
 9 clear that at some point the structure does undergo dissipative rearrangements,
 10 involving either local mechanical instabilities (particularly at low temperatures
 11 or in the ideally athermal limit) or thermal activation.

12 In understanding the connection between structure and deformation pro-
 13 cesses in amorphous materials, some familiarity with the concept of a poten-
 14 tial energy landscape is helpful. The potential energy landscape is simply the
 15 many-body potential energy of a material, expressed as a function of the atomic
 16 positions [58, 59]. Figure 7(a) is a schematic one-dimensional potential en-
 17 ergy landscape for a glass, which has many possible atomic configurations. At
 18 low temperatures we expect to find the system near one of the local minima
 19 in the potential energy landscape, which are called “inherent structures” or,
 20 more colloquially, “basins.” With increasing temperature the system can ex-
 21 plore nearby inherent structures via thermal activation over the saddle points
 22 connecting them. Transitions of this sort among closely-related configurations
 23 are associated with the fast β relaxation (inset to Fig. 7(a)).

24 The potential energy landscape of a glass-forming material also has larger-
 25 scale topography, described in terms of “metabasins” (or sometimes “megabasins”).
 26 Upon cooling through the glass transition a glass will find itself in an inherent
 27 state (A in the inset to Fig. 7(a)) in one of these metabasins. Although the
 28 glass can explore nearby configurations (B and C) via the β relaxation process,
 29 the asymmetry in barriers means that $A \rightarrow B$ transitions are more likely than
 30 $A \rightarrow C$ transitions. The system will therefore remain in the same metabasin
 31 unless a sequence of transitions to higher-energy inherent states occurs, allow-

Figure 7: (a) Schematic potential energy landscape for a glass. Upon cooling from the liquid, the system will find itself in one of the basins (A in the inset.) The β relaxation corresponds to a thermally-activated transition to a neighboring **basin** ($A \rightarrow B$) but a glass does not have enough thermal energy to transition to another metabasin by a series of uphill jumps ($A \rightarrow C$). Changing to another metabasin requires sufficient thermal energy to activate the α transition—that is, the glass must be heated through the glass transition to become a supercooled liquid again. (b) Applying a shear stress changes the shape of the potential energy landscape, possibly rendering some stable configurations unstable by eliminating the barrier to a neighboring configuration. (c) Distribution of activation energies in a simulated metallic glass before and after plastic deformation, from Ref. [60].

ing it to escape to an adjacent metabasin. This requires substantial thermal activation and is the basis of the slower α relaxation process.

For a given collection of atoms there is only one potential energy landscape, since the configuration parameter describes all 3^N possible locations of N atoms, regardless of whether the material is a liquid or a glass. Which state a material is in depends on its temperature, because temperature determines the dynamics with which the material explores the potential energy landscape. Liquids move easily between adjacent inherent states, and even to different metabasins. Glasses are essentially frozen into an inherent state, moving to a new inherent state only infrequently via a β relaxation process and never to another metabasin (on the time scale of the observations).

Atomic rearrangements associated with mechanical deformation correspond to traversing saddle points in the potential energy landscape and are connected to the two major types of relaxation processes in glasses. The primary (or α) relaxation reflects the dynamics associated with the glass transition, when a supercooled liquid vitrifies to become an amorphous solid. The secondary (or β) relaxation corresponds to atomic rearrangements on a smaller scale and is the main source of dynamics below the glass transition temperature [59, 61]. At one time it was thought that the β relaxation was only associated with intramolecular degrees of freedom (such as rotation of side groups in polymer glasses), but Johari and Goldstein showed that β relaxation occurs even in glasses composed of rigid molecules [62]. This, together with the observation of β relaxation in metallic glasses [63] (where no intramolecular degrees of freedom exist) clearly shows that this category of relaxation must be associated with collective rearrangements of atoms or molecules.

The connection to mechanical behavior arises from the effect of deformation on the potential energy landscape [64, 65]. In particular, shear deformation can cause minima in the potential energy to disappear, rendering the system unstable and forcing it to move to an alternative nearby inherent state (Fig. 7(b)). Simulations suggest that a relatively small number of atoms (10–50) participate in the mechanical instability [64, 66]. It seems clear that since both these

mechanical instabilities and the β relaxation are strongly influenced by the potential energy landscape around the particular inherent state of the glass, the two phenomena must be related in a fundamental way.

The atomic rearrangements associated with the mechanical instability of the potential energy landscape are typically called “shear transformations” following the seminal bubble raft investigations of Argon and coworkers [67, 68]. Some controversy has arisen regarding whether sites of potential shear transformations are somehow encoded in the structure of the glass. Those who hold such a viewpoint typically refer to these regions as “shear transformation zones” (STZs). If this view is correct then one could, in principle, quantify the population of STZs in some way that would describe the mechanical state of the material.

Regardless of whether sites for shear transformations are intrinsic to the structure, shear transformations occur not just in the plastic regime but quite early on in the portion of deformation typically characterized as elastic. In this regard they can result in small but measurable amounts of dissipative reversible response even at quite low strains [69]. This could arise either due to the imposed strain lowering a barrier so as to permit thermal activation, or by introducing an instability that sends the system into a lower energy state which may or may not be stable in the unstrained state. At finite temperatures this leads to rate-dependent elastic behavior—viscoelasticity or internal friction that can be measured experimentally [70]. At larger strains the shear transformations lead to irreversible plastic deformation events, as described in the next section.

4. Plastic deformation

4.1. Shear transformations

One connection between the anelastic response discussed in the preceding section and plastic deformation is a recent analysis of dynamic mechanical response, revealing evidence of distinct energies associated with STZs of discrete sizes [71–73]. This suggests a picture in which the operative STZ sizes are determined by the loading rate or, equivalently, the applied stress. For a particular

Figure 8: Quadrupolar strain fields around STZs in a colloidal glass. (a) Calculated shear strain field around an STZ modeled as an Eshelby inclusion subjected to a strain of 0.05. (b) Self-correlation function of the strain from (a), normalized to the maximum value of the self-correlation and with a color axis set to show only values of $0 \pm 10\%$ of the maximum. (c) Experimentally measured self-correlation of the strains in a colloidal glass at a strain level similar to that in (a) and (b). (Calculations and data from Ref. [85].)

loading rate there will be a particular STZ size below which the STZs can relax quickly compared to the loading rate and thus contribute to the anelastic response, while larger STZs are essentially frozen in their initial configuration until the stress becomes large enough to trigger the rearrangement. Thus, while it appears that there is a broad distribution of STZ sizes, the plastic response appears to be dominated by the portion of the distribution just beyond the reach of thermal activation on the experimental time scale.

Quite a bit of work has been done to characterize the sizes and energies of shear transformation zones by atomistic simulations [74–78], experiments on metallic glasses [79–83], and experiments on model systems, especially colloids [84, 85]. For example, Fig. 8 illustrates the shear strain field around an STZ modeled as an Eshelby-type inclusion, compared to measurements on a sheared colloidal glass. The quadrupolar nature of the strain field around the inclusion is clearly reflected in the local displacements of the colloid particles.

Several controversies about shear transformations remain, however. One issue regards the nature of the structural features that play roles analogous to dislocations in crystals. Both Argon’s shear transformation [86] and Spaepen’s flow defect [87] were conceptualized as localized plastic rearrangements. Atom-

istic simulations, particularly those performed in the flowing steady state at
low temperature or the athermal limit, however, reveal strong spatio-temporal
correlations in the deformation events [76, 88–90]. These ramified atomic rear-
rangements are prone to misidentification as shear bands, but they are different
from experimentally-observed shear bands in metallic glasses in that they are
transient and typically do not persist long enough to localize a significant strain.
Interestingly, they have quite profound effects on shear induced diffusion in the
glass that can be quantified to extract a dimensionality for these collective
events [91]. The main controversy around these observations is whether such
ramified correlated events are more characteristic of the fundamental process
by which glasses deform than the localized regions of deformation envisioned by
Argon [86], Spaepen [87] and others.

More recent investigations have revealed that even these larger events can
be thought of as localized rearrangements that exhibit the typical quadrupolar
stress signature of an Eshelby inclusion [76]. It has been hypothesized that the
long-range elastic interactions by which such objects interact may induce these
localized STZs to correlate in space and time [92]. This is likely to be more
pronounced in steady-state shear where mechanical deformation has strongly
disordered the structure of the material and the STZ density (or susceptibility
to shear transformations) is consequently high. In addition this trend may be
strongly influenced by inertial effects [93].

Another intriguing question links the elastic and plastic response of metallic
glasses: Does the linear elastic response of a metallic glass, and in particular
the phonon spectrum at low frequencies, provide any information about the
sites of plastic deformation? Schober and coworkers associated low-frequency
vibrational modes with β relaxation and demonstrated that these modes are a
combination of plane waves and localized vibrations [94–97]. More recent work
suggests a correlation between atoms that participate strongly in low-frequency
phonon modes and deformation activity, with such atoms being several times
more likely than a random atom to participate in deformation. Regions contain-
ing such atoms have been denoted “soft spots” and they appear to persist on

385 order of the α relaxation time of the sheared system, surviving multiple transi-
 tions in their vicinity [98, 99]. This is surprising because the vibrational modes
 being probed are essentially aspects of the elastic response of the glass that say
 nothing directly about the saddle points connecting the inherent states prior to
 and after the activation of an STZ. It is an open question as to whether these
 390 soft spots are STZs or whether it is better to think of them simply as “fertile
 regions” that can give rise to shear transformations. An important recent result
 is the observation that such regions appear to be susceptible to deformation
 only in certain orientations [100], indicating that STZs really are encoded in
 the structure of the glass and that the “fertile region” interpretation may be
 395 insufficient. The reason for this close linkage between linear response and the
 available structural transitions remains unclear, however.

There is now abundant evidence that a variety of properties of metallic
 glasses are heterogeneous on the nanometer scale; this include stiffness [101,
 102], yield load in nanoindentation [103], and energy dissipation [104]. The
 400 structural heterogeneity also means that the mechanical properties can be anisotropic
 on the nanoscale [105]. Recently, Ketov and coworkers showed that thermal cy-
 cling to low temperatures induced structural rejuvenation of a metallic glass [106].
 They attributed this to the thermal expansion coefficient being heterogeneous
 on the nanoscale, and it may be that the thermal expansion is anisotropic as
 405 well. The variation in thermal expansion causes local stress concentrations upon
 heating or cooling and thus irreversible non-affine atomic rearrangements, which
 in turn affect the subsequent deformation behavior of the glass. It has also been
 asserted that the structure of metallic glasses may have a significant volume
 fraction (perhaps a quarter of the total) for which the structure resembles that
 410 of the liquid even more closely than does the structure of the remainder of the
 glass [107]. Presumably the length scale of the heterogeneity is small, although
 this was not directly accessible in that study.

These observations point out a fundamental distinction between glasses and
 crystals: Crystals are, for the most part, uniform in their structure but glasses
 415 are heterogeneous in both structure and properties. Understanding defects in

crystals is of course essential for understanding mechanical behavior, but these defects can conveniently be viewed either as perturbations on the underlying uniform structure or as independent entities in their own right. An important question is whether distinct structural defects are important for understanding the behavior of glasses, where the structure is heterogeneous by its very nature and there is a distribution of structural states.

4.2. Structural evolution under load: Constitutive equations

Another area of active research, at the intersection of materials science and continuum mechanics, is the development of broadly applicable constitutive equations suitable for modeling the evolution of metallic glass under various mechanical loads and thermal histories. Early work by Argon [86] and Spaepen [87] proposed generalized constitutive forms for the activation of shear transformations or flow defects respectively, which were subsequently applied in an attempt to understand the instability that leads to strain localization (and particularly whether the instability was due to structural softening or heating) [108–110].

Any attempt to develop a generalized constitutive model faces the problem of how to describe the evolution of the structure of the glass with time. Much early work was based on the free volume model of Cohen and Turnbull [111, 112], implicitly assuming that free volume is a natural description of metallic glass structure. The viscoplastic methodology of Anand and Su, for example, relies on free volume and another empirical parameter, cohesion, which evolve monotonically towards steady-state values [113]. Shear softening and localization are observed in this model (Fig. 9) but the scale of the shear bands is limited by the finite-element mesh because there is no internal length scale. Qualitative agreement with experiments and atomistic simulations is observed [114], but like other free-volume-based methods no clear means exists to validate the internal parameters against experimentally measurable or atomistically simulated details. The model has also been used to model experimental behavior at high homologous temperatures [115] but runs into issues at low temperatures because it assumes a relatively rate-insensitive yield surface. While this avoids the dif-

Figure 9: Comparison between experimentally-observed shear band patterns resulting from plane-strain indentation of a metallic glass (top) with a contour plot the plastic strain (bottom) calculated using the constitutive model of Su and Anand [114]. (Figure from Ref. [114] and used by permission.)

difficulty of dealing with rate sensitivity it also removes any explicit connection between flow and structure. Attempts have been made to address this problem by instead incorporating a variation on the Peierls concept [116] but it is not clear this is appropriate, given that coarse-graining of STZ structure is an assumption of all such constitutive modeling.

Johnson, Lu and Demetriou [117] have proposed a free-volume-based theory for deformation and flow at high homologous temperatures. This theory relies on a self-consistent methodology and assumes disordering at a rate proportional to the plastic strain rate in competition with relaxation on time scales described by the Vogel-Fulcher-Tammann (VFT) equation. Although semi-empirical, the VFT relation gives a good fit to viscosity measurements over a wide range of temperatures in equilibrium and supercooled liquids. The resulting theory provides excellent fits to the emergence of non-Newtonian behavior in the liquid at low temperatures and high strain rates. It can also provide a means of calculating the strain rate sensitivity, which is important to evaluating the stability of flows against localization. However, the divergence of the relaxation time as one approaches the VFT temperature (which is typically significantly above room temperature) clearly limits this theory to the liquid and supercooled liquid regimes.

A different methodology which also builds upon the prior work of Argon and

Spaepen is the effective temperature STZ theory [118]. Originally developed in the context of direct comparison with low-temperature molecular dynamics simulations of glasses subjected to different stress and strain controlled mechanical loads [119], this methodology attempts to build a mean-field theory around the STZ concept of defects. The main deviation from the Argon theory is the proposition that the STZ population can be used to describe the structural state of the system. The main deviation from Spaepen’s flow defect picture is that the orientations of the defects as well as their number density are taken into account in a way that allows for the existence of a clear transition from bounded to unbounded flow at a well-defined flow stress.

Recent developments embedding the STZ theory within an effective temperature formulation have placed the theory on a thermodynamic foundation distinct from the free volume hypotheses of Turnbull and Cohen [120, 121]. In this formulation the slow structural degrees of freedom of the glass are described as a distinct sub-system separable from, and only weakly coupled to, the fast, primarily vibrational degrees of freedom that come into equilibrium with the environment on short time scales. The disorder in the structural sub-system is described in terms of its configurational entropy and energy. Since the derivative of an energy with respect to an entropy is a temperature, albeit one that may be far out of equilibrium, this permits the formal definition of an effective temperature of the structural degrees of freedom. The evolution of this effective temperature must be explicitly modeled. This equation of motion is far more constrained than the evolution law for free volume because it must represent how the mechanical work on the structural sub-system raises the energy—that is to say, it is an expression of the first law of thermodynamics. Furthermore, the second law of thermodynamics requires that the rate of dissipated plastic work is non-negative after one takes into account the fraction of potentially recoverable work, such as the work stored in anelastic deformation and defect generation. This provides guidance on how the evolution of the structural state couples to the rate equations proposed to describe the kinetics.

The assumptions of the effective temperature theory have been validated by

comparing aspects of the constitutive equation to atomistic simulations. In particular, molecular dynamics simulations of shear bands in simple 2D Lennard-Jones systems have permitted a test of the assumption that (in at least some cases) one can separate the effect of the effective temperature on flow from the effect of stress on the STZ transition rates [122]. Furthermore, numerical implementations of the effective temperature STZ theory facilitate understanding of the development of shear bands near stress inhomogeneities [123, 124] and cavitation near crack tips (Fig. 10) [125]. The theory has also been successfully applied to explain experimental investigations of materials annealed for varying times at stresses close to yield [126, 127], rheology at various temperatures near the glass transition [128], experiments regarding variable amplitude cyclic loading [129], and stress overshoots during serrated flow [130].

5. Localized plastic deformation: Shear bands

The tendency for metallic glasses to experience shear localization at temperatures well below the glass transition due to a lack of strain- and strain-rate hardening has long been recognized [5, 131]. Two excellent review articles on shear bands in metallic glasses have recently appeared [10, 132] so in this section we highlight some recent results of particular importance and seek to place them in context. Because terminology regarding shear bands is often imprecise, we adhere to the language proposed in Ref. [5]:

- *shear front* refers to a propagating front of shear displacement;
- *shear banding event* refers to the initiation and propagation of localized shear displacement, whether progressively as a shear front or by uniform deformation on a shear band;
- *shear band* refers to the approximately planar volume of material that is sheared during a shear banding event.

5.1. Nature of shear banding events

Greer, Cheng, and Ma [10] helpfully outlined three scenarios for shear banding events. The first is homogeneous nucleation, in which STZs activated

Figure 10: Numerical solution of STZ equations reveals differences in stress state (shown here as the hydrostatic stress p normalized to the yield stress in shear, s_y) ahead of a crack tip, depending on the structural relaxation of the glass as quantified by the effective temperature χ_0 . At the same overall stress intensity the stress concentration is more pronounced in a more-relaxed glass (a) than in a less-relaxed glass (b), and the crack tip morphology is different as well. These differences lead to cavitation in the more-relaxed glass (c) and ultimately to catastrophic failure (d). The crack tip morphology in (d) is similar to that observed experimentally (e). (Data for parts (a)-(d) from Ref. [125]. Part (e) is from Ref. [32] and used under the terms of the Creative Commons Attribution License.)

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9 throughout the material by an imposed stress link up when the percolation
10 threshold is reached to form a shear band. Disruption of the atomic- or medium-
11 range order on this band can lower the flow stress and allow continued uniform
12 sliding on the band. As one might expect, the stress required for homogeneous
13 nucleation is large [133] and so although it is commonly observed in atomistic
14 simulations [134], in real materials it is likely that shear banding events initiate
15 heterogeneously at stress concentrations, as seen in simulations with inhomoge-
16 neous loading geometries [135–137].

17
18 A second scenario involves initiation at a stress concentration followed by
19 propagation across the specimen of a mature shear front that carries the entire
20 shear offset associated with the shear banding event (akin to a mode II shear
21 crack). One model of this behavior, by Shimizu and coworkers [138], made
22 several specific predictions, including that the mature shear front would prop-
23 agate at approximately the shear wave speed of the glass and that it would be
24 accompanied by significant temperature increases, to at least the glass transi-
25 tion. Although this model may be appropriate for high-rate loading, it is now
26 known that shear banding events under quasi-static loading occur over time
27 scales much longer than those predicted by this model [139–142] and that, at
28 least in some situations, shear banding events occur without large temperature
29 increases [143, 144]. Furthermore, it is not clear how this model can accommo-
30 date situations in which there is a variation in shear strain along a shear band,
31 for example in bending [145] or near a mode I crack tip [146].

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33 It appears likely that under quasi-static loading shear bands form by ini-
34 tiation of a shear front at a stress concentration. The shear front propagates
35 across the specimen, disordering the atomic-scale structure along its path, low-
36 ering the local flow stress, and allowing continued deformation on the resulting
37 shear band. Under a macroscopically homogeneous strain state (such as uniax-
38 ial compression or tension) continued deformation on the shear band can occur
39 by sliding along the entire length of the shear band simultaneously, as has been
40 observed with high-speed cinematography [142, 147]. This picture is consis-
41 tent with scanning-electron microscopy (SEM) observations of fracture surfaces

that show no difference between the two ends of the shear band [10, 148]. Under other loading conditions such as bending there can be a gradient in shear offset along the length of the shear band. For example, Qu and coworkers recently showed that shear bands that form at the macroscopic yield stress and span the specimen have shear offsets that are independent of position along the band [149], presumably because the loading conditions permit plastic deformation everywhere along the band simultaneously as just described. On the other hand, they also observed that shear bands that form below the macroscopic yield stress and do not span the specimen have shear offsets that vary with position along the band. The latter case presumably arises when a shear front initiates at a stress concentration and propagates some distance away, but away from the stress concentrator there is insufficient driving force to allow continued propagation.

It has been proposed that the reduction in viscosity or flow stress associated with shear banding events is due to a stress-induced glass transition, in which the shear stress disrupts the atomic-scale structure of the glass so as to become more like the equilibrium structure in the liquid [150]. Indeed, it has been recently observed that there is a brief ($\sim 10 \mu\text{s}$) burst of acoustic emission around the onset of a load drop during serrated flow, quantitative analysis of which suggests that it is associated with a dilatation of about 2%, comparable to that which would be observed on heating to the glass transition [158, 159]. Heating due to plastic work in the shear band can reduce the flow stress or viscosity, but it is now widely accepted that this is typically a consequence rather than a cause of plastic deformation [5, 10, 137, 151]. It is important to bear in mind that heating is not an intrinsic property of shear bands, but is sensitive to extrinsic conditions including the imposed strain rate, the size of the sample, and the stiffness of the testing machine [152]. Nevertheless, in at least some cases there is little heating associated with quasi-static deformation because the time scale over which heating occurs (a few milliseconds) is comparable to the characteristic time scale for thermal diffusion ($\tau = l^2/\alpha \simeq 3 \text{ ms}$ for a diffusion distance $l = 100 \mu\text{m}$ and thermal diffusivity $\alpha = 3 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$

for Vitreloy 1, [153]) [143, 144]. There is no contradiction here with the long-standing observation of significant melting on fracture surfaces because fracture occurs on much shorter timescales (in a matter of microseconds) that allow significant heating [144] (Fig. 11). The difference in time scales implies that unstable fracture of metallic glasses is more than a simple runaway shear banding event on a single shear band. One clear difference is that fracture involves cavitation [154, 155], a subject that has recently been the focus of several computational studies [125, 156, 157].

The inhomogeneous mode of deformation by shear banding events gives way to homogeneous deformation as the testing temperature approaches the glass transition (see Fig. 19 in Ref. [5]). One controversy in the literature has been whether a transition from shear banding to homogeneous deformation also occurs as a function of sample size. Around the time of Ref. [5] several groups reported that sub-micron specimens deform homogeneously [160–162] while other groups reported shear banding even for samples as small as 150 nm [163, 164]. The literature on this subject and possible explanations for the apparent transition and the disparate results have been extensively reviewed [10, 165]. Here we draw attention to the recent work of Tönnies and coworkers, who reported that the spacing of shear bands was proportional to the diameter of their specimens, and suggested that the transition to homogeneous deformation occurs when the spacing of the shear bands becomes comparable to their thickness [166]. This explanation avoids the necessity of invoking a length scale for the transition based on a presumed nucleation size for shear bands.

From a theoretical perspective, another means of analyzing shear bands and inhomogeneous deformation has been to implement constitutive equations such as the effective-temperature STZ equations described in Section 4.2 above. Simulations of a stretched bar with a notch utilizing such a methodology have shown that in such models shear bands can grow quasi-statically from stress concentrations due to the feedback between plastic flow and disordering that arise in the material [123] and produce results similar to molecular dynamics simulations [135] and experiments [139, 142]. These methods have also provided

Figure 11: Fracture of metallic glasses in uniaxial compression occurs on much shorter time scales than shear band operation. The load drop due to a shear banding event evolves over several milliseconds (a), while fracture is over in a matter of microseconds (b). Figure reproduced with minor formatting changes from Ref. [144] under the CC BY 3.0 license.

quantitative means for analyzing the waiting time, strain rate, and temperature dependence of serrated flow in shear bands in metallic glasses [130].

5.2. Structure and properties of shear bands

The large shear strains in shear bands suggest that their structure should be different from the surrounding material, which is either undeformed or at least not as extensively deformed. Transmission electron microscopy (TEM) would appear to be an ideal choice for investigating the structure of shear bands. Most TEM studies agree that the thickness of shear bands in metallic glasses is around 5-20 nm [10, 167]. In many such studies the shear band region was thinner than the surrounding material making interpretation problematic [168, 169], but a recent study using a focused ion beam (FIB) milling lift-out technique to produce TEM specimens of uniform thickness yielded results similar to the earlier work [170].

A more fundamental problem is that the thickness of a shear band, and the structural evolution of the material within it, reflect the conditions under which it was created. An early cautionary note was provided by the observation that both the dilatation and stored energy of extensively deformed metallic glass ribbons is too large to be attributed to shear bands of this thickness, if it is assumed that plastic deformation occurs only in shear bands that leave slip steps on the surface of the specimen [171, 172]. This suggests either that shear bands are thicker than the TEM observations cited above indicate, or that plastic deformation occurs outside the shear bands.

Fundamentally, plastic deformation of any kind is a response of the sample to the displacements imposed on it. For metallic glasses the imposed displacements during plastic deformation well below the glass transition can be accommodated by shear bands ranging from single bands with extensive shear [173, 174] to a profusion of bands with minimal shear [175] or even homogeneous deformation [126, 127, 176], depending on the sample geometry and loading conditions. The most common approach to TEM studies is to form shear bands by bending thin specimens. Conner and co-workers showed that the displacement on shear

bands in a plate loaded in simple bending increases as the square of the thickness of the plate [177, 178]. Although the shear strain is probably not uniform across a shear band, it is reasonable to expect that the shear band thickness t may be proportional to the displacement u through $t = u / \tan \bar{\gamma}$ where $\bar{\gamma}$ is the average shear strain in the band. If this is true then the small displacements associated with bending a thin TEM specimen would result in thin shear bands.

There are, in fact, indications that shear bands produced in bulk specimens are thicker than those seen in TEM. For example, experiments in which a series of nanoindentations are made across the thickness of a shear band do reveal reductions in hardness [173, 174] and modulus [174] over comparatively large distances (Fig. 12). On the other hand, surface traces reveal no evidence of significant plastic flow so far from the center of the shear band (see for example the images in Ref. [144]), and a stability analysis of the differential equations governing coupled thermal and dilatational softening suggests that the characteristic thickness of shear bands should be on the nanometer scale if the softening is dominated by free volume effects [179]. It is therefore unlikely that changes in hardness and modulus over distances of a micrometer or more are a direct manifestation of structural changes due to plastic flow within a thick shear band. Far from the center of the band the plastic flow is likely quite low and would tend to appear more like a homogeneous background flow. It would not require especially large strains to affect modulus or hardness if the atomic environments were significantly disturbed, tilting the balance of the different types of clusters towards those that are GUM-like (Sec. 2). Alternatively, changes in hardness and modulus away from the center of the band may be due to residual stresses developed around a narrow shear band during deformation, or to diffusive structural relaxation after the deformation ceases.

Although atomistic simulations indicate that the extensive shearing inside a shear band disrupts the atomic short-range order of the glass [122, 134, 137, 180], detailed experimental evidence of structural evolution in shear bands is surprisingly scarce. The older literature is reviewed in Ref. [5]. More recently, it was found that shear bands formed by compression of a bulk specimen, and

Figure 12: Hardness and modulus across a single shear band measured by nanoindentation, normalized to the values well away from the shear band. Significant effects can be observed as far as 20 μm from the center of the band. (Data from Ref. [174].)

removed by FIB lift-out, showed no contrast in bright-field or high-resolution TEM images, although small changes in electron scattering patterns were observed [168]. However, a lift-out technique applied to thin ribbon specimens did yield clear contrast in high-angular dark field scanning-transmission electron microscopy images as well as electron energy-loss spectroscopy images, which were attributed to dilatation in the shear bands [170]. Similar techniques on thin-film samples prepared by electropolishing have been used to infer density variations along the length of shear bands [181]. Other recent evidence for dilatation in shear bands include density changes in cold-rolled glasses [182], enthalpy recovery from rolled specimens [182, 183], and relaxation of dilatation in a single shear band via thermomechanical analysis [173]. The observation of dramatically enhanced atomic diffusivity [184] and a preference for crystallization in shear bands [185] are also suggestive of structural disorder. Finally, we note that there is also evidence for more complex shear band structures, such as distinct inner and outer zones [186].

Broadly speaking, the experimental observations seem to be consistent with the simulation results but more work is needed to clarify the details of structural differences between shear bands and the surrounding material. It should

be noted that a highly disordered structure during a shear banding event implies rapid structural relaxation once deformation ceases, so the static structure measured after the fact in experiments provides only indirect information about the flowing state. True *in situ* studies of structural evolution inside shear bands would be desirable. These present a formidable challenge at room temperature due to the short time scales involved, but they may be possible at cryogenic temperatures where single shear bands that evolve over many seconds can be produced [187].

5.3. Dynamics of shear banding events

From a practical point of view, the dynamics of shear banding events determine whether shear banding can be a dominant mode of plastic deformation, and probably also have a strong influence on the rate dependence of fracture toughness. More fundamentally, although the fundamental mechanism of deformation (shear transformations) is believed to be the same for both homogeneous and heterogeneous deformation, the time and length scales associated with shear banding events at room temperature make experimental studies on the atomic scale difficult. But because these mechanisms (along with the loading conditions) determine the shear band dynamics, careful measurement and understanding of the dynamics can provide insights into the mechanisms of deformation.

Perhaps the most familiar manifestation of shear band dynamics is the appearance of abrupt load drops during either confined or displacement-controlled uniaxial compression, commonly referred to as serrated flow [188, 189]. In general, serrated flow can occur when the strain rate sensitivity of a material is negative because localized flow can cause the instantaneous strain rate of the material to exceed the imposed strain rate from the machine. This is symptomatic of dynamic strain aging in which the rate of plastic deformation is comparable to the rate of a thermally-activated relaxation mechanism over a limited range of strain rates and temperatures [190]. A prominent example is the Portevin–Le Chatelier effect in crystalline alloys in which mobile dislocations

Figure 13: Serrated flow (filled symbols) occurs so long as the shear displacement rate (v_{SB}) exceeds the displacement rate imposed by the crosshead velocity ($\sqrt{2}v_{XH}$, because the shear occurs at approximately 45° to the loading direction). But v_{SB} decreases with decreasing temperature so there is a critical temperature T_{crit} below which the shear displacement rate is determined by the crosshead velocity. In this case flow becomes non-serrated (open symbols) and the shear displacement rate is independent of temperature. The cross-over temperature (T_{crit}) decreases with decreasing crosshead velocity. (Figure adapted from Ref. [132] using data for $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ loaded in uniaxial compression from Ref. [192].)

repeatedly break free from and are re-trapped by diffusing solute atoms [191]. Phenomenologically, one would expect that serrated flow would disappear at low temperatures and at high strain rates if the thermally-activated relaxation mechanism cannot keep up with the imposed strain rate. This is indeed observed in the Portevin–Le Chatelier effect, has long been known for serrated flow in metallic glasses as well (Fig. 13) [188], and has been included on deformation maps for metallic glasses [5].

Shear band dynamics have been examined in an elegant series of experiments by Löffler and coworkers [132], who interpreted them in terms of the effective temperature formulation of STZ theory described above [130]. By adding a thermally-activated relaxation term to the rate equation for evolution of the effective temperature at thermodynamic temperatures well below the glass transition, they were able to use the STZ theory to reproduce several significant experimental results, including the transition from serrated to

non-serrated flow at low temperatures or high strain rates.

Serrated flow in metallic glasses is one example of a much broader class of avalanche phenomena that includes Barkhausen noise, shearing of granular materials, crumpling of paper, and dislocation-mediated plastic deformation in crystals [193]. A simple mean-field model of plastic deformation views it as the result of individual slip events (shear transformations in the case of metallic glasses) that can interact elastically to trigger a slip avalanche [194, 195]. When used to analyze the statistics of serrated flow in metallic glasses the model gives good agreement with the load drop magnitudes [189, 196] and several other statistical measures of the load drops, including duration, maximum load drop rate, and the power spectrum of the load drop rates [189]. A more stringent test is that the observed dynamics of the load drops are also in good agreement with the predictions of the model [189].

6. Strain hardening of metallic glasses

As discussed in the preceding section, shear localization in metallic glasses demonstrates an important aspect of their deformation physics: they strain-soften. This is perhaps the most undesirable intrinsic property of metallic glasses, as it limits their malleability and ductility, contributes to unstable fracture and, at least for some glasses, results in low toughness. If it were possible to evoke strain hardening, on the other hand, remarkable improvements in properties and behavior could result.

Since Ref. [5] was published there has been considerable progress in exploring the conditions under which strain hardening may be possible in metallic glasses. Broadly speaking, the progress can be categorized into two main classes of strain hardening: (i) exhaustion hardening, which is an apparent strain hardening that spans many shear localization events, and (ii) structural strain hardening, which occurs homogeneously by local stress-induced reduction of disorder in the atomic glass structure.

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770 6.1. *Exhaustion hardening: Apparent strain hardening from shear band con-*
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12 One kind of strain hardening phenomenon in metallic glasses is an “exhaus-
13 tion hardening” that develops as strain is accumulated over a sequence of many
14 shear band activations. The material inside a shear band strain softens dur-
15 ing a shear banding event (indeed, this is the cause of shear localization) so, if
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17 775 unconstrained, significant plastic strain can accumulate on a single band. On
18 the other hand, if deformation on a shear band can be arrested then the next
19 shear banding event may occur elsewhere upon further loading. What results
20 is an exhaustion hardening where the most favorable (*i.e.* the weakest) initia-
21 tion sites are the first on which shear bands form, then the next-weakest, and so
22 on [5, 197]. Even though there is no true strain hardening the apparent strength
23 of the entire specimen appears to rise because the stress required to trigger each
24 shear banding event is higher than the one before. In the limit where all the
25 “weaker” sites for shear localization are used up the glass may attain the true
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27 780 elastic limit, which has been approached in very small samples after exhaus-
28 tion of the weakest sites [198]. We call this an “apparent” strain hardening
29 because it is unlike strain hardening in crystalline metals, where the structure
30 becomes inherently more resistant to plastic flow, *opposing* strain localization
31 and therefore developing essentially homogeneously over the strained volume.
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34 The key to exhaustion hardening lies in preventing the overall plastic strain
35 of the specimen from being accommodated on a single shear band (or a small
36 number of shear bands). To do so, plastic flow on the shear band must be
37 arrested despite having already been triggered and being in the middle of a
38 self-perpetuating softening cycle.
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41 The simplest and most common way of arresting a shear band is by unload-
42 ing it; removal of the shear stress driving flow will arrest shear localization. In
43 many testing geometries, especially those that are strain controlled, shear bands
44 naturally become unloaded when their shear offset accommodates the imposed
45 strain on the specimen. An intuitive example is rolling: once the thickness of a
46 sheet has been reduced to the (fixed) separation of the rollers, no further shape
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change is mandated and the shear bands that were triggered during deformation can be arrested. Similar statements can be made about other multiaxial loading conditions such as indentation and extrusion. In fact, the earliest references to strain hardening in metallic glasses pertain to drawn wires [199, 200] where many shear bands form and are arrested geometrically. More recent work has observed the same effect in constrained compression samples, where the aspect ratio is below ≈ 1 and thus shear bands geometrically are forced to intersect the platens [201, 202], or in severe torsion where failure is proscribed [203]. As discussed above (Sec. 5.3), even in nominally load-controlled testing of specimens with large aspect ratios, dynamic effects in the loading apparatus can lead to intermittent unloading during a shear localization event.

There is also improved understanding of what constitutes an effective geometrical constraint on an active shear band. Beyond the examples of clear mechanical constraint noted above, even small geometrical imperfections such as minor misalignments or miscuts [204] or even a single void [189] in samples under nominally unconstrained loading (such as uniaxial compression) can impose a remarkable degree of constraint. Such effects can suppress failure, permit many shear bands to form, and generally lead to apparent strain hardening and extensive malleability. Taking advantage of these effects, there have been many efforts to make composite materials based on metallic glasses, where the second-phase particles provide the constraint on shear band operation [205–208]. Such composites can be tough, malleable, and ductile, but further discussion of them is beyond the scope of the present review.

While geometrical constraints are an important approach to the arrest of shear banding events, in other cases arrest can be accomplished under nominally unconstrained loading, apparently due to structural changes that emerge at large shear strains within the shear band. The shear-driven nucleation of crystallites in shear bands has now been widely reported and several groups have shown that this could be associated with apparent strain hardening in samples where many shear bands formed [197, 209–211]. In some glasses that already contain nanocrystals the extensive plastic flow on a shear band causes the particles to

coalesce and align, resulting in strain hardening [212]. Both the nucleation of crystalline regions and their alignment and coalescence in shear were suggested to be important in locally hardening the shear bands at such large strains; this
835 paves the way to their arrest and triggering of secondary shear bands, such as is required for the exhaustion hardening mechanism. Additional means of energy dissipation are also available to the crystalline phases once they do appear, such as twinning or martensitic transformation [213], which can further help to slow, bifurcate, or arrest shear banding events.

840 If shear banding events can be arrested after finite strain, continued plastic deformation will require triggering of new events, which may occur either on existing shear bands or on newly-formed bands. In the latter case it becomes possible to produce material with a high volume density of shear bands. Examples of this include the early work on wire drawing mentioned above [199, 200]
845 along with constrained compression, rolling, and severe plastic deformation processing [203, 214, 215]. The influence of extensive prior plastic deformation on the response of the material to subsequent testing can be complex. On the one hand, plastic deformation within a shear band disrupts the structure of the glass. This renders the material both softer and more compliant around individual
850 shear bands [173, 174] and tests which average over both shear bands and undeformed material also show a reduction in hardness due to prior plastic deformation [201].

An alternative behavior results from exhaustion hardening and points out the importance of loading geometry. Extensive inhomogeneous plastic deformation
855 of a metallic glass produces a material with a wide distribution of structural states. Some material likely remains virgin or nearly so; some has been transected by a single shear band; and some, lying at shear band intersections, has been multiply shorn. The wide spectrum of local strengths in the material offers ample opportunities for triggering shear banding events. If the loading geom-
860 etry favors initiation on previously-existing shear bands then the strength of the material will be reduced due to work-softening in the bands, as mentioned above. But a mismatch between the loading geometry and that of the prior

deformation can require a new set of shear bands to form. For example, although a rolled glass sustains many shear bands that are oriented to permit the shape change imposed by rolling, these bands are not necessarily oriented to facilitate deformation in other geometries. The sample might need to form new shear bands which further transect the material and its many local structural states, opening the door to exhaustion hardening. In an elegant series of experiments illustrating this principle, Takayama measured the tensile fracture stress of metallic glass ribbons heavily deformed by rolling, as a function of the angle between the tensile axis and the prior rolling direction [216]. If the loading geometry was such that plastic deformation occurred on previously-existing shear bands then the fracture stress was reduced relative to undeformed material, in accordance with expectations based on work softening in the shear bands. However, samples tested in tension at large angles ($> 40^\circ$) with respect to the rolling direction—such that shear banding events did not occur on the shear bands produced by rolling—showed an increase in fracture stress, even above that of the undeformed material. Takayama speculated that shear band intersections cause hardening in a manner similar to dislocation intersections in crystals, but since shear bands are not physical defects with restoring line tension it is not clear that this analogy holds. Instead, the pre-existing shear bands may tend to favor shear in directions unfavorable for the new loading geometry, potentially deflecting the new shear bands and thus geometrically hardening the glass.

More broadly speaking, the fact that glasses have a heterogeneous local structure with a complex universe of possible arrangements provides interesting opportunities for the control of shear bands. Many authors have noted that a distribution of local strengths arising from a heterogeneous structure is desirable because it promotes a distribution of shear bands in metallic glasses [209, 210, 217–219]. This is an area needing additional research if we aspire to intentionally evoke exhaustion hardening by control of the local states.

6.2. Strain hardening of the glass atomic structure

Whereas exhaustion hardening as described above is about the progressive shearing of different spatial regions of a bulk glass specimen, there is a second potential mechanism for strain hardening in metallic glasses that is more like conventional strain hardening as it is known in crystalline metals and alloys. The mechanism is based on mechanically-driven relaxation of the glass structure, and is a genuine strain hardening, as it *opposes* strain localization and therefore can occur homogeneously. For simplicity we term it “structural strain hardening” to differentiate it from exhaustion hardening.

In some sense, structural strain hardening of metallic glasses has been known for a much longer time. It is a common part of the language of glass mechanics at high temperatures, where the two notional processes that regulate mechanical behavior—shear-induced disordering and diffusional reordering or relaxation—are both active. Because the structural reordering process is thermally activated, at high temperatures it is entirely possible for deformation to be dominated by this diffusional process, which increases density and (presumably) structural order and strengthens the glass. This genuine structural strain hardening is most commonly appreciated during “stress undershoots”, situations where a deforming glass is subjected to a sudden load drop, whereupon the diffusional reordering of the glass leads to a transient strengthening—that is, strain hardening—which occurs homogeneously (Fig. 14) [220].

Although the two processes of shear-induced disordering and diffusional reordering are both active at all temperatures, the general view has been that structural relaxation at low temperatures is slow. This allows the shear-induced disordering process (also sometimes thought of as a free volume-creation process) to dominate, leading to shear localization. Structural relaxation is still important because it affects the characteristic time scale for shear banding events [132] but under ordinary (uniaxial) loading conditions it cannot suppress shear localization entirely.

Recently, however, Wang and coworkers were able to achieve structural strain hardening in a Zr-based glass at ambient temperature [222]. Those authors

Figure 14: Data from strain-rate-drop experiments during homogeneous deformation in the non-Newtonian flow regime of $\text{Zr}_{41.25}\text{Ti}_{13.75}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$. At each strain rate the structure (and therefore the flow stress) reaches a steady state. When the strain rate is suddenly reduced there is a sudden drop in flow stress which is followed by structural ordering and strain hardening. Data from Ref. [221].

studied notched tensile specimens with a high stress triaxiality, and showed that the large hydrostatic tensile stresses promoted diffusional relaxation of the glass more than it did shear yielding. The result was a notch region that elongated significantly *in tension* without any shear localization, stabilized by the strain hardening process. They also explicitly demonstrated hardening in the specimen in the notch region with hardness tests as shown in Fig. 15. It appears that the glass was demonstrably hardened during plastic flow due to a local relaxation process promoted by the hydrostatic tensile component of stress.

This shows that some metallic glasses are capable of structural strain hardening under tensile loads, and most importantly, around notches and crack tips where stresses are concentrated and triaxiality is high. The implications of this mechanism for fracture have yet to be fully explored, but strain hardening around the crack tip is clearly highly desirable to increase fracture toughness. Wang and coworkers suggested that the ability of a glass to strain harden by stress-enhanced diffusional relaxation at a crack tip may be a determinant physical aspect separating brittle from tough glasses [222].

Figure 15: High aspect-ratio notches in tensile specimens promote strain hardening and plastic flow. (a) Hardness measured across the notched region of a specimen deformed to 7% plastic strain, compared to hardness of undeformed material. (Data from Ref. [222].) (b) *In situ* x-ray radiographs of a notched specimen in the unloaded state (top) and loaded to 2.4 GPa true stress (bottom). The extension of $h - h_0 = 77 \mu\text{m}$ corresponds to an engineering strain of 22.5% in the notched region.

Structural strain hardening at low temperatures is also suggested by studies using nanoindentation to probe the elastic limit of metallic glasses [103, 223, 224]. Packard and coworkers showed that in several different glasses, applying a nominally elastic load with a hard indenter led to local hardening. After first loading the glass in the elastic range and demonstrating full strain recovery on unloading, they measured the yield point on a subsequent reload cycle as the point where the first shear band was triggered and unrecoverable strain recorded. Using hundreds of data points in a statistical approach, they showed that elastic loading could cause a hardening by 20-30%. STZ dynamics simulations as well as atomistic simulations [224, 225] provided support for the interpretation that around a stress concentration (such as the indenter tip, or perhaps a crack tip), local atomic-scale rearrangements are plausible before macroscopic yield is triggered and shear localization occurs.

Interestingly, cyclic loading appears to be particularly effective in producing these local atomic rearrangements with concomitant effects on the mechanical properties of the glass. For example, in the work cited above Packard and coworkers also showed that cyclic loading in the elastic regime could progressively evoke strain hardening [225]. The implications of this for fatigue of metallic glasses would appear to be significant, but we are not aware of any studies of local hardening around fatigue crack tips as yet. The discovery of Ketov and coworkers, cited above, that thermal cycling to cryogenic temperatures causes structural rejuvenation, would appear to be a related effect [106].

It is worthwhile to note that the indentation studies and the notched tension experiments described above demonstrate structural strain hardening of metallic glasses for loading configurations with significant stress concentrations, and a similar comment could be made about the inhomogeneity of properties believed to be behind the cryogenic cycling effect. This underscores a need for greater understanding of STZs and related atomic structural changes in glasses under complex loading states in heterogeneous structures.

7. Directions for future research

Throughout this review we have tried to emphasize connections between the structure of metallic glasses and their mechanical behavior. From an experimental point of view, such connections are frustrated by the difficulty of obtaining precise, atomic- and nano-scale structural information about an amorphous material. In atomistic simulations we have perfectly precise information, but we lack quantitative descriptors of the key structural features that influence deformation behavior. In concluding this review we expand on these issues, identifying areas for research that are critically important for expanding our understanding of metallic glasses and which, on the basis of work to date, seem ripe for fruitful exploration.

- One critical question is the establishment of criteria for unambiguous identification of STZs—presuming, of course, that such defects are encoded in the structure of glasses. This is critical for testing the predictions of micromechanically-based constitutive laws and would open up the possibility of experimental verification of various metrics for identifying STZs. We note recent attempts to apply machine learning methods to automate the relation of structural measures to deformation activity [226]. This presents another promising area, particularly if the diagnostics derived in this way can be reverse-engineered to understand the origin of the connection between structure and defects.
- A related question is characterization of the spectrum of potential inelastic events that are available to the STZs in a given glass structure. Presumably these events range from mostly shear-like to mostly dilatational, with few being purely one or the other. A detailed, tensorial elaboration of the STZ spectrum at both the saddle point configurations and the final post-transition states would be of great interest. We see promise in using MD simulation and emerging structural characterization techniques (discussed below) to test predictions of constitutive models about the evolution of

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1000 structure; direct comparisons between simulations and experiments are possible but will require new coarse-graining schemes and careful validation. Extending the analysis to different states of structural relaxation would provide great insight into some of the more complex issues associated with shear localization and fracture.

1005 • It would also be desirable to develop quantifiable connections between constitutive theories and thermodynamic concepts. Experimentally this should be possible through calorimetry on macroscopic and microscopic specimens. Simulation methods that permit exploration of complex energy landscapes could in principle provide direct quantitative measures of configurational entropy by allowing the enumeration of the basins that comprise a meta-basin. In doing so, concepts like effective temperature become calculable and the predictions of theories that make reference to them directly testable.

1010 • To date, studies of metallic glass deformation have emphasized uniaxial stress states. But studies of behavior and structural evolution under complex states of loading are urgently needed, for example to elucidate the processes of shear localization and fracture. The flow of shear momentum and free volume through the glass structure are clearly linked, but the details of this linkage and its role in controlling the balance of ordering and disordering are not well established. The elaboration of localization will require detailed and coupled understanding of these issues under multiaxial loading conditions. Much as studies of homogeneous deformation under uniaxial loading contributed to the development of a quantitative STZ theory, quantitative experimental work exploring multiaxial flow in the homogeneous regime could provide crucial input on these more complex issues.

1015 • The fracture process itself is obviously of immense importance but as yet of limited understanding. But there is a relative paucity of information on fracture because *in situ* structural observations are difficult (due to the

length scales and time scales involved) and because the heat released may significantly alter or destroy structural details that might reveal the evolution of the crack tip. This is an area where simulation may provide insights

more readily than experiments. The relatively poorly-understood process of cavitation in glasses is a promising area for materials theory, because the inherent heterogeneity of the material on the smallest scales implies that the traditional separation between heterogeneous and homogeneous nucleation of cavities does not easily apply.

- Continuing advances in structural characterization are likely to improve our understanding of the structure of amorphous materials, including metallic glasses. For example, electron scattering techniques are being used to study atomic clusters in metallic glasses [227, 228] and nanometer-scale structure and heterogeneity [181, 229]. More speculatively, the development of sources of spatially-coherent x-ray sources, already being used to probe the three-dimensional structure of nanocrystals, could ultimately provide the ability to resolve the atomic-scale structure of metallic glasses [230]. At this point, knowing position of every atom in the structure, experimentalists would face the same problem currently posed by atomic simulations: What to do with all that information?

- Even with existing techniques there are opportunities for significant advances in structural characterization. The importance of structural heterogeneity has been discussed above, so mapping of structure and properties on the nanometer scale is likely to be fruitful. Clever *in situ* experiments are also possible. For example, it has been shown that single shear bands evolve on time scales of seconds during deformation at cryogenic temperature, as opposed to millisecond time scales typical of deformation at ambient temperature [187]. This ability should make it feasible to study the atomic-scale structure around the advancing shear band using x-ray scattering, or the evolution of the macroscopic shear band structure using x-ray imaging (assuming the shear bands provide sufficient contrast).

We close by noting that much of the enthusiasm for bulk metallic glasses began about two decades ago with major advances in alloy design which in turn led to innovations in metallic glass forming and processing science. Many of the more detailed mechanical studies that have so dramatically enhanced our understanding of the behavior of metallic glasses were made possible by those advances, and we expect that further developments in glass forming and processing could facilitate study of the remaining issues. For example, we need to better understand how glass chemistry and cooling rate influence structure and therefore mechanical properties. A related issue is how plastic deformation leads to rejuvenation and strain hardening. Understanding these issues would go a long way towards enabling the use of metallic glasses in structural applications.

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Metallic glass
structure

Shear transformations

Plastic deformation