

Simulating the mechanical response of amorphous solids using atomistic methods

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Abstract. The study of elasticity, plasticity and failure in non-crystalline solids has greatly benefitted from the application of atomic scale simulation. This “colloquium paper” reviews the ways in which a variety of computational approaches have been used to elucidate the atomic scale phenomena that control the mechanics of amorphous solids. The constitutive theories that have been developed for describing mechanical response are briefly reviewed, as well as the prospects for testing the assumptions of these theories using simulation. We list what we believe to be the most pressing open questions for substantiating these theoretical approaches, and ultimately for understanding and predicting the mechanical responses of amorphous solids.

1 Introduction

Every known class of materials, metallic, polymeric, ceramic or otherwise, can exist in an amorphous state in which the atoms exhibit liquid-like structure although the material response is distinctly that of a solid. While the processing, structure and properties of this amorphous solid state have long been studied by various experimental means, scientific understanding remains phenomenological. The result is that theory gives little guidance as to how to design, characterize and deploy new amorphous materials to meet societal needs.

The reason for this gap in our understanding of a rather large class of materials is that amorphous materials present daunting challenges both experimentally and theoretically. Just as Tolstoy observed that, “all happy families resemble one another; every unhappy family is unhappy in its own way,” crystals conform to common ordered structures, while the disordered arrangements of atoms in amorphous solids are unique. Importantly, this does not mean that amorphous solids lack structure. The structure of an amorphous solid is determinant of its properties and strongly dependent on its thermo-mechanical history. Evidence shows that this structure is ever-evolving. Experimental techniques for measuring the salient details of amorphous structure are just now emerging, and remain challenging to implement and interpret.

A great deal of attention has been devoted to the nature of the glass transition, wherein a liquid, through a continuous decrease in temperature, becomes an amor-

phous solid. Considerable experimental and simulation work has been performed in this area, far more than can be adequately reviewed here. It is important to point out that while a fundamental understanding of the glass transition remains a grand challenge, there are many other routes by which amorphous solids can be produced. For example, high rate or ion-assisted deposition also often result in amorphous films. Much work needs to be done before we are able to connect the physics by which a glassy material is generated to the resulting properties of that material.

The focus of this “colloquium paper” will be the mechanical response of amorphous solids, and, in particular, the role of simulation in the study of these properties. Atomic scale simulation methods have proven particularly useful for developing insight into the structure and mechanical response of amorphous solids in the absence of detailed structural data from experiment. We will review the simulation work that has been undertaken to date with an eye toward pointing out the conclusions that have been drawn from these approaches so far and the outstanding questions that have yet to be sufficiently addressed.

2 Background: mechanics of materials

The prediction of mechanical response of materials is a well-established area of engineering and applied mathematics with an extensive literature [1–5]. Such prediction is accomplished through the construction of constitutive theories that relate the strain of the material, i.e. the portion of the displacement gradient not accounted for by translation or rigid rotation, to the history of forces

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to which the material has been subjected. These forces, which are typically imposed at a boundary, influence the strain via the stresses they induce in the material.

Most classical continuum constitutive theories make little or no reference to the underlying structure of the material in question. Elasticity gains its wide applicability from the fact that a small number of empirically measured coefficients can provide extensive predictions of the reversible response of materials to induced stresses. However, once a material is pushed past the reversible elastic regime into the plastic regime of irreversible deformation, reliable predictions become more difficult. Many canonical theories, like the widely used von Mises yield criterion and various hardening relations that have been used to model how a material's strength changes as it deforms, limit their predictions to cases that are rate and history independent in order to make the problem tractable without requiring an excessive number of arbitrary assumptions. In reality plastic response can be extremely sensitive both to rate of deformation and to the material's thermo-mechanical history. This reflects the fact that while elastic behavior is typically homogeneous and uniform on small scales, plasticity typically arises from the generation, propagation and motion of defects on the atomic scale. These defects often interact in important ways with material microstructure on many intermediate length and time scales.

In the context of crystal plasticity a type of line-defect known as a dislocation mediates plasticity. A thorough understanding of dislocation processes and interactions has led to new mesoscale methodologies for modeling plasticity on the dislocation scale in single crystals [6–8]. These methodologies hold out great promise for testing both established [9] and novel theories of dislocation plasticity in crystalline materials [10]. We are only now reaching a comparable level of understanding of the processes that control deformation in amorphous solids. Creating adequate constitutive theories and mesoscale models for deformation in these materials requires a more adequate elucidation the underlying molecular mechanisms by which non-crystals accommodate deformation and the thermodynamic laws that govern these processes [11].

3 Early micromechanics and simulations

Mechanical properties, and particularly plastic deformation, have received more attention in the context of metallic glasses and polymers than in covalently bonded solids. In particular, metallic glasses, promising for structural applications and relatively simple to simulate, have received the most attention. The earliest theory of deformation in metallic glasses was the flow defect model developed by Spaepen [12] based on the “free volume” formalism pioneered by Turnbull and Cohen [13]. In order to extend these theories by providing a more detailed mechanistic picture of the atomic scale rearrangements, Argon and co-workers painstakingly tracked the motions of bubbles in two-dimensional bubble rafts to simulate the response of a metallic glass to shear deformation [14,15]. This appli-

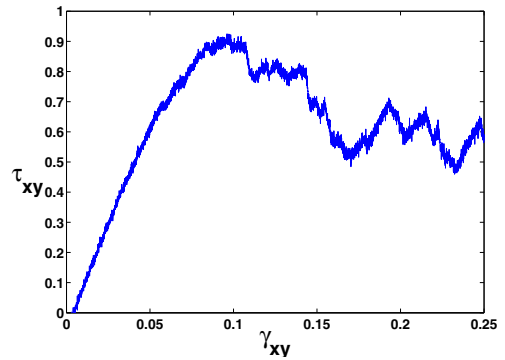


Fig. 1. The shear stress versus shear strain response at constant strain rate of a 10240 atom 50:50 binary Lennard Jones alloy modeled using the Wahnstrom parameterization [18].

cation of analog simulation presaged the widespread use of numerical simulation for such purposes, and led to the identification of localized rearrangements that they characterized as shear transformations. These investigations provided the impetus for Argon's proposed model for plastic response in amorphous solids [16].

Numerical simulation in the field started with two dimensional modeling of amorphous metals by Maeda and Takeuchi [17]. They observed the hallmarks of plastic flow in simulations of amorphous solids: perfectly plastic or shear softening mechanical behavior during which discontinuous drops in the potential energy and stress are accompanied heterogeneous rearrangements of atoms that appear to be localized in space and time. Figure 1 shows a curve from a more recent simulation of a 50:50 composition binary alloy simulated using the Wahnstrom parameterization of the Lennard Jones potential [18]. Both the shear softening behavior and stress drops are evident here. In follow-up work with Kobayashi, Maeda and Takeuchi linked rearranging regions to fluctuations in the stress field [19]. These investigations were extended by Srolovitz et al. [20,21] who systematically searched for a predictive structural signature for regions susceptible to shear deformation. Their conclusion was that regions of anomalously high shear stress, denoted tau-defects, were more likely to undergo deformation than the surrounding medium while other properties such as local density, pressure, etc. did not correlate with deformation activity.

Further simulation studies were undertaken by Deng et al. [22–25] investigating glass formation, relaxation kinetics and deformation response. In particular, these studies looked carefully at the evolution of topology in two-dimensional structures by examining the distribution of 5-, 6- and 7-fold coordinated atoms. A number of other salient observations including the existence of pronounced Bauschinger effects were also noted in these studies.

These early simulation approaches established the canonical hypotheses that have served as the foundation for the development of constitutive theories of amorphous solids.

- Spaepen’s hypothesis that the number of deformable sites is related to a quasi-thermodynamic structural parameter, the *free volume*, based on the work of Turnbull and Cohen.
- Argon’s observation that *shear transformations* are localized events involving a few tens of atoms.
- The idea promulgated by Maeda et al. and further pursued by Srolovitz et al. that these shear transformations take place at particular regions in the material, which are structurally distinct.

4 Simulation methodology

To simulate a metallic glass at the atomistic level, one first prescribes the interactions between the atoms. These interactions may incorporate details of the quantum chemistry between the various atomic species, or they may be based on a more phenomenological approach. In phenomenological approaches, one often uses simple pair-wise interactions. This choice is very much in the spirit of Argon’s pioneering work [14,15] using soap bubbles to search for generic phenomena which are primarily sensitive to features such as the sizes of various atomic species but much less sensitive to other details of the underlying chemistry.

Once the interactions are specified, one still needs to specify equations of motion for the particles. If one is interested in the response to applied shear, the simplest procedure is to continually minimize the potential energy as the system is deformed. The use of this simple technique in glasses dates back to the seminal work by Maeda and Takeuchi [26]. In these so-called quasistatic simulations, the issue of shear rate is subtle and often misunderstood. On one hand, the simulation corresponds to a physical system which is being sheared rapidly, as the simulation gives no chance for thermal relaxation as the strain is imposed. On the other hand, the simulation corresponds to a physical system which is being sheared slowly, as the simulation gives infinite time for mechanical relaxation after the imposed shear strain triggers some plasticity. It seems reasonable that physical systems which are at low enough temperature such that thermal relaxation is effectively absent and are being sheared at the limit of vanishing strain rate are in this regime. These quasistatic simulations should be a good representation of the dynamics in this regime.

To go beyond the quasistatic simulations to address the affects of finite shearing rate and finite temperature, the most obvious choice is to perform conventional molecular dynamics (MD) [27]. In MD simulations, one integrates Newton’s equations of motion given the interaction forces. In a physical system, local plastic relaxation results in a release of energy which is eventually converted into heat. In an isolated Hamiltonian system, this heat would accumulate, raise the temperature, and melt the sample. MD simulations deal with this problem by imposing an artificial damping which mimics the affects of a thermal reservoir into which the excess heat can flow [27].

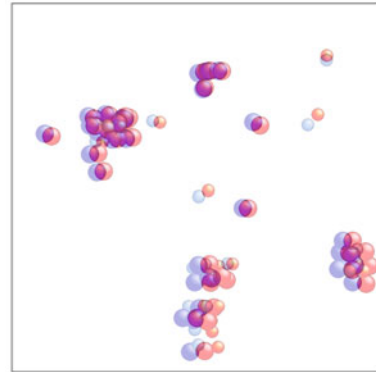


Fig. 2. Atoms with an environment exhibiting greater than twice the imposed 5% strain in their immediate neighborhood. Blue spheres show the locations of atoms before the imposition of the strain, and red spheres are the positions after imposing the strain. This data is from the same simulation used to create Figure 1.

5 Plasticity at the atomistic scale

There are two different kinds of characterization typically performed in analyzing simulation data on the atomistic scale. The first kind characterizes the changes induced in the structure by an applied strain or stress. Such measurements are inherently comparative. That is to say that they quantify the change in positions of atoms from the initial to the final structure. Consequently such measurements do not have meaning in the absence of some well defined reference state. This includes measurement of displacement fields performed in the simulation work mentioned above.

Examining displacement fields per se is not ideal for characterizing mechanical deformation because atoms can be displaced by translation or rotation without inducing elastic or plastic deformation. Displacement gradients and, more specifically, strains are more relevant for deducing where the material has undergone deformation. Falk and Langer [28] proposed a method to extract the best fit linear strain and, in doing, also quantified a parameter D_{min}^2 which measured the degree of non-affine rearrangement in a region of material. This non-affine portion of the displacement field represents displacements not accounted for by the uniform field and may arise due to elastic rearrangements on smaller length scales or plastic discontinuities. Figure 2 shows clusters of atoms in regions of anomalously high strain from the same three-dimensional system simulated to produce Figure 1. The atoms shown are those for which the local strain environment exceeds twice the imposed strain of 5%. Figure 3 is a closeup of the rearranging cluster of atoms in the lower right hand corner of Figure 2.

While it is important to characterize the deformation patterns in simulation, it is equally important to characterize the local structure in a way that is not dependent on a predetermined reference state. This has been attempted in a number of different ways. The tau-defect analysis by Srolovitz et al. represent one such attempt at structural characterization via analysis of the residual stresses in the

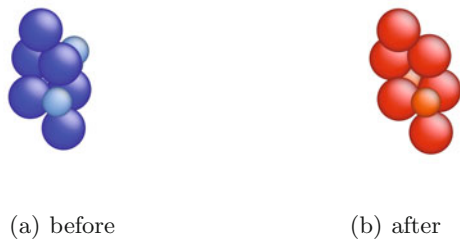


Fig. 3. A closeup of the rearranging cluster of atoms in the lower right hand corner of Figure 2.

as-quenched glass structure [21]. Other structural parameters that have been measured in order to gauge their ability to predict incipient plastic flow include potential energy [29], density [30], short range order [31–35], percolation of short-range order [36–38], and various definitions of free-volume [37,39–41].

5.1 Heterogeneity in dynamical and mechanical response

In the late 1990’s, various workers [42–45] observed that structural rearrangements in simulations of deeply supercooled glassforming liquids organize into complex spatio-temporal patterns. This so-called dynamical heterogeneity was subsequently observed in experiments on colloidal glasses [46]. This organization gives rise to anomalous, non-Fickian, single-particle displacement statistics and has been related to anomalous, stretched exponential structural relaxation [47–49].

Yamamoto and Onuki went beyond the earlier work by incorporating shear into their simulations [50]. For the unsheared systems, they found that the extent of spatial correlations grew with decreasing temperature, T , up to the lowest temperatures at which they could equilibrate their system. For finite strain rate, $\dot{\gamma}$, they found that the spatial extent of the correlations grew as the strain rate decreased, saturating at the thermal equilibrium value. This led them to conjecture that the $T = 0, \dot{\gamma} = 0$ point acted as a critical point in the $(T, \dot{\gamma})$ parameter space with an associated growing correlation length.

Later, Maloney and Lemaitre [51,52] and Tanguy et al. [53] performed simulations using an athermal quasistatic protocol to study the $T = 0, \dot{\gamma} \rightarrow 0$ behavior. This new work employed the same basic methodology of the seminal studies by Maeda and Takeuchi [26] and later work by Srolovitz et al. [20], but with a new focus on identifying spatio-temporal correlations in the structural rearrangements. It demonstrated that an avalanching mechanism proposed by Bulatov and Argon was controlling the dynamical heterogeneity in zero temperature deformation [54]. In Bulatov and Argon’s view, elasticity would couple local rearrangements. Although an isolated rearrangement would lead to a global stress drop, it would lead to a spatial redistribution with both increases and decreases in stress in its neighborhood. This load redis-

tribution mechanism would lead to avalanches, much as in other systems like elastic fronts advancing in a random pinning potential or crack tips advancing through a material with heterogeneous toughness [55]. In Bulatov and Argon’s model of a structural glass, local rearrangements organized into lines of slip inclined, roughly, 45 degrees away from the principal stress axes. The athermal quasistatic simulations showed that this basic mechanism does indeed operate in real atomistic models. Other coarse-grained models based on Bulatov and Argon’s original picture showed much the same behavior [56–58]. Recent molecular dynamics studies have indicated, however, that finite strain rate and temperature impose cutoffs on the size of the plastic events and decrease the strength of stress fluctuations [111,112].

The organization of local stress relaxations into lines of slip in zero temperature shear appears to be quite different from the motions observed in the unsheared supercooled liquids where particles move along string-like features. This is not entirely surprising. The supercooled liquids are globally isotropic, while the stress in the sheared systems breaks that isotropy. Despite these differences, some consequences of the heterogeneity are common to both: a short-time regime with an exponential distribution of particle displacements crossing over to a diffusive regime with a Gaussian distribution at later times [53,59], pointing to a rather generic origin of the anomalous displacement statistics.

5.2 Relation between elasticity and plasticity

One of the most promising routes to identifying a relationship between local structure and plastic response lies in the local elasticity of the material. The atomic-level stress can be defined in a straightforward way through the Irving-Kirkwood definition [27]. In a system with pair-wise interactions, the expression reduces to

$$\sigma_{\alpha\beta} = \frac{1}{V} \sum_{\langle ij \rangle} f_{ij\alpha} r_{ij\beta} \quad (1)$$

where V is the volume of the system, $f_{ij\alpha}$ is the force between atoms i and j , $r_{ij\beta}$ is the separation between i and j , and the sum is taken over all pairs, $\langle ij \rangle$. However, a definition of the local elastic moduli is less straightforward and necessarily depends on the length scale over which one wishes to define the moduli.

The first studies of the local elastic properties of a structural glass go back to Srolovitz et al. [20,21] who studied the local atomic moduli. These moduli represent the increment in stress on that particle when its neighborhood is subjected to a homogeneous deformation. In theoretical mechanics, this assumption of homogeneous deformation and neglect of inhomogeneous elastic deformation is known as the Cauchy-Born rule. Specializing to the case of a pair-wise interaction and simple shear in the x - y plane, the expression for the Born stiffness is given by:

$$\mu_B = \sum_{ij} r_{ij} \left(r_{ij} c_{ij} - f_{ij} \right) \left[\frac{x_{ij}^2 y_{ij}^2}{r_{ij}^4} \right] + r_{ij} f_{ij} \left[\frac{y_{ij}}{r_{ij}} \right]^2$$

where c_{ij} is the second derivative of the energy with respect to separation. The information encoded in the atomic-level moduli is completely local and insensitive to any inhomogeneous, co-operative elastic relaxations which may occur when deforming a region which is larger than the neighborhood of a single particle. The spatial average of μ_B gives the Cauchy-Born expression for the modulus of the entire assembly, and it is well known that this is only an upper bound on the true elastic modulus of the system which is typically some substantial fraction below the bound.

Collective, inhomogeneous, rearrangements may lead to lower moduli than those computed assuming a homogeneous deformation. Tanguy and co-workers performed some seminal studies on the inhomogeneous elastic deformations which lead to these reduced moduli [60–62]. These studies found that the particle motion organized into vortex-like patterns with a characteristic lengthscale of roughly 30 particles. Similar observations were made for both Lennard-Jones glasses and models of amorphous Silica [63]. Maloney later argued that, as long as the disorder in the system is spatially uncorrelated and the energy eigenmodes of the system can be approximated as planewaves, then the inhomogeneous deformation should have a characteristic lengthscale which is roughly 1/3 of the system size and scales with the size of the system [64]. Goldenberg et al. used a local coarse-graining scheme to separate the displacement field into a homogeneous component and inhomogeneous component in a scale-dependent way [65]. In this work, strong localized fluctuations in the inhomogeneous component became apparent even for very small coarse-graining sizes.

So far we have discussed two extremes: atomic-level moduli under the Cauchy-Born rule and system-level moduli allowing for full inhomogeneous relaxation. To determine moduli at an intermediate scale, there are two basic routes: via dynamical fluctuations at finite temperature or via the zero temperature linear response [66]. In either case, the notion of modulus only has a well defined meaning after a coarse-graining scale is defined over which the fluctuations are averaged or the zero temperature linear response is computed.

Yoshimoto and coworkers [67] used the fluctuation formulae to study the local moduli in a polymeric glass. In Figure 4, we show such a spatial distribution of moduli defined over a meso-scale coarse-graining length. They found that the distribution of moduli became very broad for sufficiently small coarse-graining lengths. Below this coarse-graining scale, many regions had *negative* moduli, being stabilized by the stiffer surrounding regions. They conjectured that the elastically soft regions would participate most actively in plastic relaxation but the initial study was limited to the elastic regime. Locally floppy regions have been shown to give important contributions to structural relaxation in unsheared supercooled liquids [68]. The locally soft modes play an important role in dictating anomalies in the density of states [69–71], and it is natural to expect that they also play a role in plastic relaxation under shear.

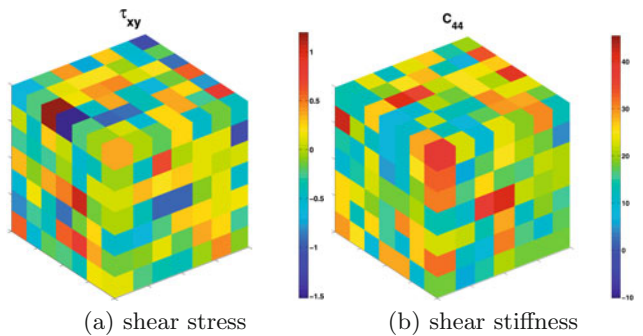


Fig. 4. The simulated system now analyzed by subdividing the simulation cell into equally spaced regions and measuring shear stress and shear stiffness.

Tsamados and co-workers have used an explicit coarse-graining scheme to define moduli at a meso-scale [72]. In their framework, the system is strained at zero temperature and allowed to fully relax. The stress and strain field are then independently coarse-grained. They found that, for small enough globally applied strain, the local stress and strain fields are always in a linear relationship, and they define the meso-scale moduli as the proportionality constant between the coarse-grained stress and coarse-grained strain. The main finding is that meso-scale regions of low moduli are strongly correlated with regions which undergo plastic rearrangement. Unfortunately, the authors were unable to extract any characteristic length-scale for the low moduli regions, and this issue remains an outstanding puzzle. In our opinion identifying a characteristic length-scale for defects in structural glasses is a crucial step in identifying the elementary mechanisms of plasticity.

6 Constitutive theories

6.1 Free volume theory

The goal of studies of the mechanical properties of amorphous materials is two-fold. The first goal is to understand how the instantaneous state of the system influences the materials' response to shear stress. As such both the work by Spaepen [12] and Argon [16] proposed a common relation between strain rate, the current *free volume* and the applied stress that arises from previous work by Eyring [73],

$$\dot{\gamma} = f \exp\left(-\frac{1}{\chi}\right) \exp\left(-\frac{\Delta G}{k_B T}\right) \sinh\left(\frac{s \Omega}{k_B T}\right). \quad (2)$$

Here $\dot{\gamma}$ is the shear rate; f is an attempt frequency; χ is a ratio between the *free volume*, v_f and the *excess free volume* needed for a region to be susceptible to shear, V^* ; ΔG is the excess free energy needed to effect a transition in the absence of an applied deviatoric stress, s , and Ω is an activation volume.

On its own equation (2) is insufficient to describe the flow of the material since the structure of the amorphous

solid evolves during shear. It is also necessary to describe how the state of the system evolves during deformation. To this end both theories provide a differential equation for the rate of change of the *free volume*, v_f . These equations were based primarily on physical arguments regarding the rates at which *free volume* would be created and destroyed during shear.

6.2 Shear transformation zone theory

Since that time a number of additional constitutive theories have been proposed that make somewhat different assumptions about the processes that govern how the microstructure of the amorphous solid evolves. Most closely related to the approaches by Spaepen and Argon is the *shear transformation zone* (STZ) theory by Falk and Langer [28]. In the context of STZ theory a *shear transformation zone* is a region of the material susceptible to *shear transformation* under a suitably applied shear stress. The primary difference between this theory and the earlier theories is that the orientations of the *shear transformations* are considered to be essential to the theory. This orientational nature is evident in MD simulation by the fact that different regions of the material deform under application of differently oriented shear stresses. It is also evident in the induced anisotropy and Bauschinger effects observed first by Deng, Argon and Yip [25]. This requires revising the standard Eyring equation given in equation (2) so that it accounts for STZs of varying orientation. In a one-dimensional scheme this would lead to a flow rate expressed in the form

$$\dot{\gamma} = [n_+ R(s) - n_- R(-s)]. \quad (3)$$

Here n_+ and n_- represent the normalized population density of STZs oriented in two different perpendicular orientations. In the STZ picture the transition rates R must be provided either in the standard Eyring form given above where $R = \exp[-(\Delta G - s\Omega)/k_B T]$ or in another form suitable for describing deformation when $k_B T \ll s\Omega$. In addition the equations of motion of the STZ distribution must include the evolution of the orientation; so, the equations of motion are different for n_+ and n_- . In the context of STZ theory the evolution of this orientational degree of freedom gives rise to a true yield stress in the low-temperature limit. Although the earlier Spaepen and Argon theories have an exponential dependence of shear rate on stress, they do not exhibit the dynamical transition from bounded to unbounded plastic flow that arises naturally in the STZ theory.

The STZ theory builds upon the earlier work by Spaepen and Argon in another way as well. The theory includes terms that relate to the annihilation and creation of STZs during flow. These rates are both proportional to the rate of dissipation and their ratio is set by a parameter [28]. In the original version of the STZ theory this parameter was held constant, but in subsequent development of the theory this becomes a dynamical quasi-thermodynamic parameter referred to as the *effective temperature*, T_{eff} [74,75]. The *effective temperature*

plays the same role *free volume* does in the earlier theories by Spaepen and Argon. However, the thermodynamic interpretation of T_{eff} provides additional means to constrain the dynamics of this important degree of freedom and to relate it to the rate of energy dissipation [11]. Simulations by Haxton and Liu have resulted in recent progress relating the steady state value of T_{eff} to the imposed strain rate at low temperatures [75,76].

STZ theory has been compared directly to the deformation and non-linear rheology of metallic glass at temperatures near the glass transition temperature [74,77]. Comparisons have been made with shear reversal during granular flow [78]. It has also been compared to data from simulations of deforming silicon [79,80]. Some of the predictions of the theory have also been tested in the context of localization, as will be discussed below.

6.3 Soft glassy rheology

Another particularly interesting constitutive theory that bears both similarities and differences from the STZ theory is the theory of *soft glassy rheology* (SGR) originally developed by Sollich and Cates [81–83]. The main difference between these models is that while STZ theory presupposes that the regions of deformation have a typical size, SGR theory proposes that there is an evolving distribution of such regions in the material. This is done by assuming that each element is drawn from a distribution of local strains l and yield energies E . This probability distribution of strains and yield energies evolves in time according to a master equation of the form

$$\frac{\partial}{\partial t} P(E, l, t) = -\dot{\gamma} \frac{\partial}{\partial l} P - \Gamma_0 e^{-[E - (1/2)kl^2]/x} P + \Gamma(t) \rho(E) \delta(l) \quad (4)$$

where $\dot{\gamma}$ is the macroscopically imposed strain rate; Γ_0 is a constant attempt frequency; k is an effective spring constant that relates the local strain l to the elastic energy threshold E , and ρ is the distribution from which yield energies of newly created regions are chosen. The parameter x plays the same role as an effective temperature in the STZ model. While the original version of SGR contains a fixed effective temperature, recently effective temperature dynamics have also been considered in the context of the SGR theory [84]. The SGR model completes equation (4) by providing a closure that relates the yielding rate $\Gamma(t)$ to the transition rate of the regions in the form,

$$\Gamma(t) = \Gamma_0 \int dE dl P(E, l, t) e^{-[E - (1/2)kl^2]/x}. \quad (5)$$

The macroscopic stress is then calculated by integrating over the local strains, such that

$$\sigma(t) = k \int dE dl P(E, l, t) l. \quad (6)$$

As with STZ theory there emerges a true yield stress that corresponds to a dynamical boundary between jammed

and flowing steady states, and the theory is generalizable to a tensor form [85] that includes orientational degrees of freedom. The SGR model reproduces many of the observed phenomena typically associated with soft glassy materials including linear response, responses to step strains and aging.

While STZ and SGR make predictions for the entire stress-strain curve given a particular thermomechanical history, a number of other investigations have sought to focus on quantifying the age and strain rate dependence of the strength, the peak in the stress-strain curve [86–88]. In particular work by Rottler and Robbins proposed a notably simple relationship based on MD simulation studies. Similarly, the pressure and/or normal load dependence of the flow stress has been an area of considerable investigation. Simulations have been carried out to investigate the degree to which the flow stress of metallic glasses are pressure sensitive, and whether they exhibit a Mohr-Coulomb like behavior [89,90]. More recently MD investigations in the metallic glass literature have extended to the effect of alloy composition on the material strength [35,91].

6.4 Shear banding

When subjected to stresses in excess of their strength metallic glasses undergo an instability that leads to the formation of shear bands. Subsequent plastic deformation occurs within very thin regions which are only tens of nanometers thick. It has long been known that many materials including steels can undergo such localized deformation due to feedback between heat release during deformation and thermal softening. Such mechanisms have been proposed for metallic glasses, but metallic glasses exhibit these instabilities even during rather slow loading. A number of experimental studies have been undertaken to determine whether thermal softening is a reasonable explanation for this phenomenon. The most convincing studies indicate that while significant heating occurs at late stages of deformation this is a consequence, not a cause, of localized deformation in these materials [92].

A number of simulation studies have been performed in order to understand the origin of the shear banding instability in amorphous solids. Some of the earliest reports of shear bands in simulation were by Varnik et al. [86,93] who observed shear bands in steady state during simple shear of a binary Lennard-Jones system. The shear bands in these cases were always found near the rigid walls of the simulation cell, and were observed to switch between the top and bottom walls of the shear cell. A number of other MD simulations have also reported shear banding in uniaxial tension [30,36,94], uniaxial compression [37,95], indentation [96,97] and periodic simple shear [29,98]. Quite different results are seen in simulations depending on the boundary conditions. In particular simulations that impose out-of-plane periodic boundary conditions, akin to plane strain, often exhibit shear banding [37,95,97] while simulations performed on cylindrical samples exhibit necking rather than shear band formation [94] depending on the details of the preparation of the surface [113].

These simulation studies have resulted in a number of important observations regarding the structural changes that accompany and possibly lead to the shear banding instability. It was observed that localized strain was favored in the low strain rate limit only for samples quenched sufficiently slowly, and this cross-over in mechanical response has been shown to correlate with percolation of a backbone of short range order in a number of systems [36–38]. In addition the shear banded region has been used to test the *effective temperature* STZ theory. In particular, analysis was carried out to test if there is a Boltzmann-like relation between a quasi-thermodynamic *effective temperature* and the shear rate. This was shown to hold over several orders of magnitude of the strain rate [29].

The existence of these MD results permits the direct comparison of atomistic and continuum numerical results based on particular theoretical assumptions. In this regard Manning et al. carried out a stability analysis and numerical study of shear banding within the STZ context [99,100]. The parameter regime was determined by comparison to the previously mentioned simulation studies [29]. These analyses indicate clearly that shear banding within the STZ model is a non-linear instability, and that materials with lower initial *effective temperature*, larger fluctuations and, to a lesser degree, higher strain rates are more susceptible to shear banding.

7 Conclusion

Simulation studies have substantially clarified a number of aspects of the atomic scale origins of deformation in amorphous materials. We have detailed some of these instances here, but we must note that in the above discussion we have focused primarily but not exclusively on simulations of metallic glasses. Important theoretical and simulation work has also been carried out in the context of polymers [101–106] and covalently bonded glasses [107–110] and though these systems deviate in interesting ways from the behavior of glassy metals, the methodologies and observed phenomena bear a striking similarity.

It seems clear from the simulations performed to date that local regions of rearrangement do arise that have quadrupolar elastic symmetry, and that the rearrangements typically increase the disorder in the glass leading to phenomena such as shear banding. However, a number of important questions remain, and simulation is likely to be even more critical in addressing these open questions.

Primary among these open questions, it remains to be clearly shown that the regions where rearrangements occur correspond to distinct local structural entities, which we have called STZs. Alternately we could imagine that STZs only exist in some more loosely defined average sense. In this scenario the plastic activity is more properly thought of as arising via stochastic events that could be triggered at any location, the direction and location of which depends in some statistical way on the thermomechanical history of the material.

The observations of collective events that trigger multiple rearrangements and can span significant length scales

also raise important questions. It remains to be determined whether these collective phenomena are critical to understanding shear flow in amorphous materials in general. Some work has been undertaken to determine how these collective events are suppressed at finite shear rates [111] and at finite temperatures [112]. It remains unclear to what extent such phenomena are a feature of steady state flow that may be suppressed before the material has reached a steady state.

Key to many of the discussions regarding constitutive theories are questions regarding which quasi-thermodynamic variables are predictive of mechanical response, and how these quantities should properly be measured. Some success has been seen using effective temperature concepts to relate potential energy per atom to shear rate via a Boltzmann like formalism [29]. However, analysis of silica systems has shown that at the rates typical in molecular dynamics these quasi-thermodynamic theories may break down [79,80]. Collecting significant statistics at lower strain rates and over longer times appears necessary to directly test some of the assumptions built into these constitutive theories.

There remain numerous fundamental questions that need to be addressed regarding the mechanical responses of amorphous solids. Creative ways of extending simulation and using it as a bridge between experiment and theory will certainly play a role in unraveling these mysteries.

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