

# Relating metallic glass mechanical properties to liquid structure

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## Abstract

Molecular dynamics simulations indicate that the mechanical properties of a model metallic glass depend critically on the degree of supercooling attained in the liquid prior to vitrification. A well-characterized binary glass-forming system roughly analogous to ZrTi was quenched instantaneously from a series of liquid temperatures. These temperatures ranged from approximately twice that of the onset of supercooled liquid behaviour down to just above the mode-coupling temperature ( $T_{MCT}$ ). The low-temperature mechanical properties of these glass samples is studied in simple shear at constant strain rate while the density of the system is held constant. All the glasses exhibit an initial linear response at small strain and approached a steady-state flow regime at large strain. However, glasses obtained by quenching from supercooled liquids just above  $T_{MCT}$ , which we will refer to as  $T_{MCT}$  glasses, exhibit higher shear strength and modulus than glasses obtained by quenching from higher temperature liquids. The  $T_{MCT}$  glasses also exhibit pronounced shear softening. The change in pressure during shear is markedly different in these glasses, and indicates that the  $T_{MCT}$  glasses retain aspects of the quenched-in structure out to as much as 25% strain. The changes in pressure also indicate significant structural changes occur even during nearly linear stress–strain response.

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## 1. Introduction

While metallic glasses have been produced since 1960 [1], recent advances in the design of bulk glass forming alloys have opened the door to the utilization of bulk metallic glass for structural applications [2]. To this end, a number of researchers have undertaken the characterization of the mechanical properties of these alloys as a function of their composition and cooling history [3–12]. These investigations have included a number of homogeneous deformation experiments carried out at constant strain rate. The goal of these investigations is the prediction of the mechanical properties of new alloy systems and the dependence of these properties on the means of preparation of the glass. However, the lack of a theoretical underpinning by which plasticity can be precisely attributed to well characterized deformation mechanisms limits our predictive capability. Argon and Shi [13] and Spaepen and coworkers [13,14] proposed the seminal micromechanical theories of metallic glass deformation. These theories are based on the notion

of locally rearranging regions that we will refer to here as “shear transformation zones” (STZs) after Argon. These theories were recently extended by Falk and Langer [15] to provide a description of the constitutive behaviour of these solids that include state-variables that are directly related to the number densities and orientations of the STZs. In addition the molecular dynamics (MD) investigations by Falk and Langer built on previous computational studies characterizing the deformation mechanisms in amorphous model materials subjected to shear [16–25]. Lacks and coworkers have made significant progress relating these unit deformations to soft modes that can be extracted by normal mode analysis [26,27]. The investigation detailed here is a direct extension of recent work by Utzet et al. which investigated the structural transitions that take place in a sheared glass [28]. As in their study we will investigate the response of a number of carefully prepared glasses to shear. However, in this work we will attempt to relate the shear behaviour to the liquid state structure by equilibrating at several liquid temperatures and then instantaneously quenching these liquids into glasses for mechanical testing.

A computational study of the connection between metallic glass mechanical behaviour and processing is timely given recent advances characterizing the dynamics that

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accompany the onset of the glass transition [29–31]. Investigations like those of Donati et al. [29] have demonstrated that spatially heterogeneous dynamics become evident in the liquid as it enters the supercooled regime. We are interested in determining whether these heterogeneities are frozen into the glass after a very fast quench and, if so, whether these heterogeneities are related to the structures that control deformation and visco-elastic shear response in the glassy solid state.

We consider the mechanical properties of a model glass-forming system that has been studied extensively in its liquid state in the context of the aforementioned studies of the glass transition [32,33]. In this system the temperature of the onset of supercooled liquid behavior is well characterized as are the mode coupling temperature and other signatures of the approach to the glass transition from the liquid state. This investigation considers a series of glasses produced by quenching nearly instantaneously from liquids over a range of initial liquid temperatures. These initial liquid temperatures vary from just above the mode coupling temperature to far above the onset of supercooled liquid behaviour. At each temperature we created 10 independent glass samples and tested each in simple shear at a constant strain rate. The stress versus strain and pressure versus strain behaviour of these samples reveals a qualitative change in the mechanical response.

## 2. Simulations

The simulations described here were carried out on a binary glass-forming system of 8000 particles in a 50:50 A:B mixture. The mass ratio between the two species is 2:1. The equilibrium BB interatomic separation is 5/6 of the AA equilibrium separation. The AB separation is the arithmetic mean of the AA and BB distances. At their equilibrium separations all bond strengths are chosen to be equal. The energy scale for this investigation is taken to be this bond strength. The length scale is taken to be the AA equilibrium bond length, and the mass scale was taken as the mass of the A species.<sup>1</sup> If we assume that the system we are simulating is an approximant of the ZrTi alloy system then these units approximately correspond to a length unit of 0.3 nm, a mass unit of 90 amu, an energy unit of 0.4 eV, a time unit of 0.46 ps, a temperature unit of 4640 K and a pressure/stress unit of 2.4 GPa [34].

In keeping with the previous simulations of this system [32,33] all results reported here were obtained from runs at a constant number density of 1.298 in the above units. This density corresponds to a mass density of approximately 5460 kg/m<sup>3</sup>, in keeping with what would be expected by applying a rule of mixtures to Zr and Ti densities in their

crystalline solid state at 1 atm pressure. However, as we will see these simulations are, in fact, carried out under extremely high pressures, approximately 5 GPa. This choice of pressure, although artificial, was made in order to enable direct use of previous simulations that characterized the onset of the glass transition in this particular system. The onset of supercooled liquid behavior in this system is known to occur at approximately 1.0 (4640 K), the mode coupling temperature is approximately 0.59 (2740 K) and the Vogel–Fulcher temperature is 0.48 (2230 K). The value of the Vogel–Fulcher temperature gives a lower bound for the glass transition temperature in this system at this pressure. These temperatures are significantly higher than would be expected in the alloy at atmospheric pressure.

The molecular dynamics simulations described here were carried out at constant temperature and strain rate. The temperature was maintained using a Nose–Hoover thermostat with a relaxation time scale of  $\tau_T = 0.1$  in dimensionless time units. In the simulations at constant strain rate standard non-equilibrium MD techniques were employed. The simulation cell was allowed to shear using Lees–Edwards periodic boundary conditions [35] and the SLLOD equations of motion [36] which can be rewritten as Eq. (1)–(4) below where the position of particle  $n$  is denoted as  $\mathbf{r}_n$ , the momentum as  $\mathbf{p}_n$ , the mass as  $m_n$ , and the force on this particle as  $\mathbf{F}_n$ .  $\mathbf{R}_0$  is a six arbitrarily chosen origin of the simulation cell, and  $\zeta$  is a dynamical variable that acts as a time-varying viscosity in order to control the temperature in the Nose–Hoover scheme. The strain rate,  $\dot{\gamma}$ , is zero during quenching and a constant during the mechanical tests in simple shear.

$$\dot{\mathbf{r}}_n = \frac{\mathbf{p}_n}{m_n} + [\dot{\epsilon}](\mathbf{r}_n - \mathbf{R}_0) \quad (1)$$

$$\dot{\mathbf{p}}_n = \mathbf{F}_n - ([\dot{\epsilon}] + \zeta[I])\mathbf{p}_n \quad (2)$$

$$\dot{\zeta} = \frac{1}{\tau_T^2} \left( \frac{\langle KE \rangle}{3/2kT_{\text{ext}}} - 1 \right) \quad (3)$$

$$[\dot{\epsilon}] = \begin{bmatrix} 0 & 0 & 2\dot{\gamma} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (4)$$

Each glass sample investigated was created by instantaneously quenching from a liquid that had been equilibrated at a temperature above the mode coupling temperature. The length of the equilibration at each temperature was several multiples of the time for the coherent intermediate scattering function to decay to zero. To ensure equilibration we also checked that there was no aging of dynamical quantities such as the mean square displacement. Once equilibrium was established, we performed a production run of length  $b\tau_\alpha$ , where  $\tau_\alpha$  is the relaxation time of the coherent intermediate scattering function calculated at the wavevector  $q_0 \approx 7.5$  corresponding to the maximum of the static structure factor. Here,  $b \approx 10^3$  for the highest temperatures and  $b \approx 190$  for the lowest temperatures studied.

<sup>1</sup> Note that these units are somewhat different from those employed by Wahnstrom [33] who scaled quantities with respect to the smaller B species.

Independent samples extracted from these liquid runs for quenching were separated by a time interval of at least  $\tau_\alpha$ .

Each of these independent liquid samples was then quenched instantaneously to a temperature of 0.2 (930 K) by reassigning velocities to each particle from a Boltzmann distribution characteristic of this temperature. Subsequent to this instantaneous quench the system was allowed to age for 10 time units (4.6 ps). This ageing time was chosen such that the potential energy of the system would no longer change rapidly on the time scale of interest for the subsequent mechanical testing. Fig. 1 shows typical curves of potential energy versus time during the ageing period from each of the liquid temperatures investigated. Oscillations are observed in the first 2 time units (1 ps) but at later times the potential energy appears to decrease monotonically. As expected, ageing continues indefinitely in the glass held at finite temperature. After this ageing period shear was imposed on the glass at a strain rate of  $10^{-4}$  (22% per ns).

### 3. Observations

At each temperature 10 independent liquid samples were quenched into glass samples for mechanical testing. The shear stress versus strain results in Fig. 2 are averages over these configurations. Error bars on the glasses quenched from the highest and lowest temperature liquids show the standard deviation from the mean quantity due to sample-to-sample variation in properties. Several common features are present in all the stress versus strain curves. Each curve has some regime of nearly linear stress–strain response at low strain. The apparent shear modulus can be extracted from the slope at zero stress, and it varies inversely with the liquid temperature prior to quench. Glasses quenched from high temperature liquids have a shear modulus of approximately 23 (55 GPa), while the glass quenched

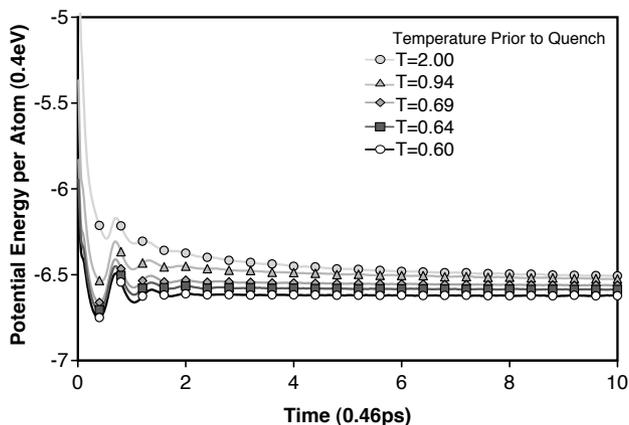


Fig. 1. The potential energy per atom during a series of quenches from liquid temperatures  $T = 2.0$  (lightest), 0.94, 0.69, 0.64 and 0.6 (darkest) to a final  $T = 0.2$  in a system where the Vogel–Fulcher (glass transition) temperature is  $T_{VF} = 0.48$ .

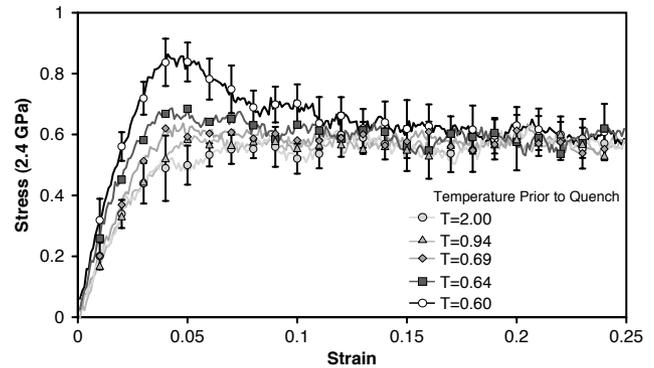


Fig. 2. Stresses measured during constant strain rate tests performed in simple shear. Each curve is an average of 10 independent samples that were quenched instantaneously from the same liquid temperature to  $T = 0.2$  prior to the shear test. The initial liquid temperatures were  $T = 2.0$  (lightest), 0.94, 0.69, 0.64 and 0.6 (darkest). The error bars on the  $T = 2.0$  and 0.6 curves show the sample-to-sample standard deviation in the data. All curves show elastic perfectly plastic behavior with the exception of the glasses quenched from the liquids closest to the mode coupling temperature  $T_{MC} = 0.59$ . These glasses also exhibit a significantly increased shear modulus.

from closest to the mode coupling temperature has a modulus of 32 (77 GPa). Each sample approaches the same steady-state flow stress at large strain, approximately 0.58 (1.4 GPa), within the sample-to-sample variation of the data.

In addition to the systematic change in apparent shear modulus, a number of other trends are evident in Fig. 2. The lower the temperature of the liquid from which the glass was quenched, the higher the shear strength of the glass, reaching 0.86 (2.1 GPa) or 50% above the flow stress, for the glass quenched from the lowest temperature liquid. Shear softening results when the shear strength exceeds the flow stress.

In addition to a change in the shear stress versus strain behaviour depending on sample preparation, there is a significant change in the pressure versus strain behaviour of the material. This occurs because the samples are held at constant volume, and hence constant density, throughout the shear test. Fig. 3 shows that the initial pressure is strongly dependent on the temperature of the liquid from which the glass was quenched. After straining, the pressure is nearly independent of the preparation of the sample, but for the samples quenched from the lowest temperature liquids, dependence on the initial condition appears to persist even out to 25% strain. The approach of the pressure to its steady-state value does not appear to be monotonic for the glasses quenched from low temperature liquids. In all cases, even those in which the initial pressure is lower than the steady-state pressure, the pressure initially decreases with strain. For glasses quenched from high temperature liquids the most dramatic changes in pressure occur in the first 2% of strain, while the stress strain response is still nearly linear. The glasses quenched from lowest temperature liquid change

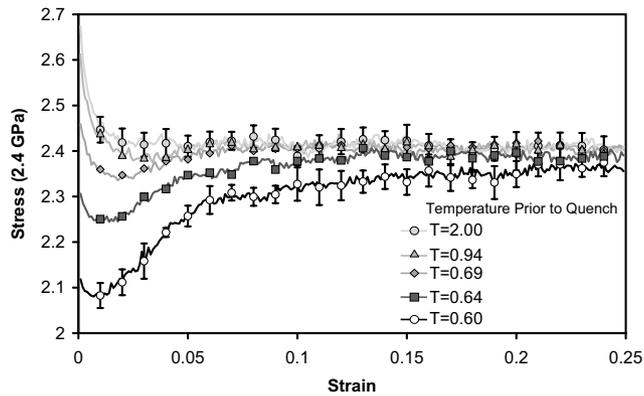


Fig. 3. The pressure measured during the constant strain rate tests. Each curve is an average of 10 independent samples that were quenched instantaneously from the same liquid temperature to  $T = 0.2$  prior to the shear test. The initial liquid temperatures were  $T = 2.0$  (lightest), 0.94, 0.69, 0.64 and 0.6 (darkest). The error bars on the  $T = 2.0$  and 0.6 curves show the sample-to-sample standard deviation in the data. The glasses quenched from the lowest temperature liquids exhibit non-monotonic behavior and an increase in pressure while the other glasses exhibit a decrease in pressure. The lowest temperature glasses do not reach the steady-state pressure even after 25% shear strain.

in pressure most dramatically from 2–6% strain. Most of this change in pressure occurs well before the onset of shear softening.

#### 4. Conclusions

The above simulations indicate that the shear modulus and ultimate shear strength of a metallic glass depend sensitively on the degree of supercooling the liquid experiences prior to vitrification. Both the modulus and strength of these glasses appear to increase sharply as their precursor liquids approach the mode coupling temperature. Glasses that undergo significant supercooling as liquids display dramatically higher strengths and exhibit marked shear softening that is absent from the glasses quenched abruptly from high temperature. Glasses maintained at constant density during shear exhibit non-monotonic changes in pressure that imply that non-monotonic changes in density that may be expected to occur in isobaric tests. The effect of the initial preparation is evident in the pressure response even at strains of 25% for glasses that spend significant time near the mode coupling temperature. Shear softening is accompanied by a significant increase in pressure during shear while perfectly plastic behaviour is accompanied by a significant decrease in pressure during shear. To a large extent these changes in pressure occur at small strains while the stress–strain response is rising in a nearly linear manner. This suggests that dramatic structural changes are taking place prior to the onset of significant plastic flow in the glass.

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