A Universal Criterion for Plastic Yielding of Metallic Glasses with a \((T/T_g)^{2/3}\) Temperature Dependence

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Room temperature \((T_R)\) elastic constants and compressive yield strengths of \(\sim 30\) metallic glasses reveal an average shear limit \(\gamma_r = 0.0267 \pm 0.0020\), where \(\tau_y = \gamma_r G\) is the maximum resolved shear stress at yielding, and \(G\) the shear modulus. The \(\gamma_r\) values for individual glasses are correlated with \(t = T_R/T_g\), and \(\gamma_r\) for a single glass follows the same correlation (vs \(t = T/T_g\)). A cooperative shear model, inspired by Frenkel’s analysis of the shear strength of solids, is proposed. Using a scaling analysis leads to a universal law \(\tau_{CT}/G = \gamma_{C0} - \gamma_{C1}(t)^{2/3}\) for the flow stress at finite \(T\) where \(\gamma_{C0} = (0.036 \pm 0.002)\) and \(\gamma_{C1} = (0.016 \pm 0.002)\).

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For a dislocation free crystal, Frenkel [1] calculated the theoretical shear strength by assuming cooperative shearing obtaining \(\tau_y \approx G/5\). The yield strength of metallic glasses is thought to be determined by the cooperative shearing motion of atomic clusters termed shear transformation zones (STZ’s) [2–5]. Compressive strengths of \(\sigma_T \sim 0.02Y\) are observed with a weak dependence on normal stress or pressure [6,7]. Here, we report elastic constants and compressive yield stresses for \(\sim 30\) metallic glasses. Yielding at \(T_R\) can be described by a critical shear strain \(\gamma_c = 0.0267 \pm 0.0020\); a better description of \(\gamma_c\) includes a dependence on the dimensionless temperature \(t = T/T_g\). A cooperative shear model (CSM) is introduced that predicts a temperature dependent \(\tau_c\) (or \(\gamma_c\)) having a “\(T^{2/3}\)” form. The CSM is based on the concept of inherent states (IS) and potential energy landscapes (PEL) developed by Stillinger et al. [8,9], Wales et al. [10,11], and Milanod and Lacks [12].

Table I shows measured density, ambient \(T\) elastic constants \(Y, G, B, \nu\) (Poisson’s ratio), yield stress in compression, \(\sigma_T\), elastic strain limit \((\sigma_T/Y)\), and glass transition temperature, \(T_g\), for \(\sim 30\) metallic glasses [13–29]. Note that \(\sigma_T/Y\) varies over the range 0.014 < \(\sigma_T/Y\) < 0.022. Ignoring the small normal stress dependence of the shear yield strength [6,7,13,14], one can plot \(\nu\) vs \(G\) \((\nu = \sigma_T/2G)\) to find the corresponding elastic shear strain limit as shown in Fig. 1. We obtain linear correlation with a best fit of \(\gamma_c = \tau_y/G = 0.0267 \pm 0.0020\), but there remains significant scatter in \(\gamma_c\). Examination shows that glasses with low \(T_g\) tend to exhibit smaller \(\gamma_c\) than those with high \(T_g\). Consider the reduced temperature, \(t = T_R/T_g\). We plot \(\gamma_c\) for each individual alloy vs \(t\) (open circles) in Fig. 2. The plot includes data (filled circles) for the temperature dependent \(\tau_y\) of Vitreloy 1 (fixed \(T_g\) and varying \(T\)) by Lu et al. [13], low temperature data for bulk La55Al25Cu20 [30] (squares), melt spun ribbons of Pd85.5Si14.5 [31] (stars), and Fe40Ni40P14B6 [31] (horizontal triangles), and bulk Pd77.5Cu3Si16.5 [2(b),24] (vertical triangles). The data for ribbons were “normalized” to obtain agreement with other data at \(T = 0\) K (\(G\) was not known for the ribbons). The “peak flow stress” of Vitreloy 1 vs \(T\) (from \(T_R\) to above \(T_g\)) was taken as \(\tau_y\). Figure 2 shows that \(\gamma_c\) is a systematic function of \(t\).

Following Frenkel, the elastic energy of an STZ is here described by a periodic elastic energy density vs strain:

\[ \phi(\gamma) = \phi_0/2[1 - \cos(\pi\gamma/2\gamma_c)] = \phi_0 \sin^2(\pi\gamma/4\gamma_c) \]  

(1)

with a minima at \(\gamma = 0\), a barrier at \(2\gamma_c\) (\(\gamma_c\) is the yield strain), and a total barrier energy density \(\phi_0\). The critical yield stress is \(\phi_0^{1\text{max}} = \pi\phi_0/4\gamma_c\). For the unstressed solid, \(G = \phi_0/\gamma_0\) giving \(\phi_0 = (8/\pi^2)G\gamma_c^2\). The “free enthalpy” density of the stressed STZ is \(h(\gamma) = \phi(\gamma) - \tau_\gamma\). In an unstressed solid, the total potential energy barrier for an STZ is \(W = \phi_0\xi\Omega = (8/\pi^2)G\gamma_c^2\xi\Omega\), where \(\Omega\) is the actual volume of the STZ defined by the plastic “core,” and \(\xi\) is a correction factor arising from matrix confinement of a “dressed” STZ [2,32]. For a Gaussian shaped strain fluctuation with core diameter \(\sigma\), one can estimate \(\xi \sim 2-4\) and \(W \sim 3\Omega \phi_0\). The details of \(\xi\) depend on the shape and size of the fluctuation and the elastic constants \(G\) and \(\nu\) for the material.

For an infinite crystal of indistinguishable atoms, the periodic minima of \(\phi(\gamma)\) are equivalent; i.e., there is no configurational entropy. For a glass, there are \(\Gamma\) stable atomic configurations or inherent states (IS’s) [8,9,33] with \(\Gamma = \exp(N\Delta s_c)\), where \(N\) is the number of atoms in the STZ, and \(\Delta s_c\) the configurational entropy per atom of the IS’s or “basin denumeration function” [9,33]. While \(\Delta s_c\) is well defined in the thermodynamic limit \(N \rightarrow \infty\), it decreases [9,10,33] for small \(N\). The characteristic strain \((\gamma_c)\) or “configurational displacement” separating neighboring configurations will increase for \(N \sim 100\) or less. On the other hand, the total barrier \(W\) also scales with STZ volume \(\Omega\) (or \(N\)). Therefore \(W \sim \gamma_c^2\Omega\) is expected have a minimum for some intermediate \(N^*\). We estimate that \(N^*\) is likely of order \(\sim 100\) atoms. Yielding occurs when the applied stress causes a critical density of “minimum” barrier STZ's to become unstable.
The barrier at finite $\tau$, $W_\tau$, approaches zero as $\tau \rightarrow \tau_C$. It is easily shown that $\phi_{0\tau}$ (barrier energy density at finite $\tau \rightarrow \tau_C$) decreases as $\phi_{0\tau} \sim (\tau_C - \tau)^{3/2}$ while the shear modulus (at finite $\tau$) $G_\tau \sim (\tau_C - \tau)^{1/2}$. The strain difference between the energy minimum and barrier configuration (saddle point) scales as $\delta \gamma_\tau \sim (\tau_C - \tau)^{1/2}$ as $\tau \rightarrow \tau_C$. Mechanical instability of the STZ at $\tau_C$ takes the form of a "fold catastrophe" [11,34]. For $\tau \rightarrow \tau_C$, the parameters $W_\tau = \phi_{0\tau} \gamma_\tau \Omega_\tau$, $\delta \gamma_\tau$, and $G_\tau$, are related by the scaling law

$$\frac{\phi_{0\tau}}{(G_\tau \delta \gamma_\tau)^2} = R = 1/4,$$

so that $W_\tau = G_\tau \gamma_\tau^2 \Omega_\tau$.

where $R$ is the "fold ratio." Wales et al. [11,34] have shown that, for binary Lennard Jones (LJ) glasses (256 atoms) and liquid salt clusters (71 atoms), this scaling relation holds on average, even far from $\tau_C$. For the Frenkel landscape of Eq. (1), $R$ actually varies from 1/4 to $\pi^2/32$ as $\tau$ varies from $\tau_C$ down to 0. Analysis of simulation results [12] for shear induced destabilization of individual IS's of a 500 atom LJ glass shows that Eq. (2) is obeyed (within 10%) over $0 < \tau < \tau_C$. Assuming scaling holds on average:

$$W_\tau = W_0(T)[(\tau_C - \tau)/\tau_C]^{3/2} = \phi_{0\tau}[(\tau_C - \tau)/\tau_C]^{3/2} \xi \Omega_\tau = 4RG_{0\tau} \gamma_\tau^2[(\tau_C - \tau)/\tau_C]^{3/2} \xi \Omega_\tau,$$

where $G_{0\tau}$ is the shear modulus of the unstrained glass which includes a weak dependence on $T$ (Debye-Grueneisen thermal expansion) for a fixed glass configuration. The scaling law holds for any function $\phi(\gamma)$ for which $d^2\phi(\gamma)/d\gamma^2$ is analytic around the inflection point. At finite $T$ and applied $\tau$, thermal strain fluctuations will carry the system over the barrier $W_\tau$. For plastic flow to occur on a given time scale (or strain rate $\dot{\gamma}$), the rate of barrier crossing must reach a critical value comparable to $\dot{\gamma}$. Using

$$\frac{\tau_C}{\tau} = \frac{\pi^2}{32}.$$
Equation (6) for the yield stress becomes

\[ \sigma_y = \sigma_0 \exp(-W_\tau/kT) = C\dot{\gamma}, \]  

(4)

where \( \sigma_0 \) is a dimensionless constant of order unity, and thus

\[ W_\tau/kT = -\ln(C\dot{\gamma}/\sigma_0) = \frac{4RG_0T\gamma_C^2[(\tau_{C0} - \tau_{CT})/\tau_C]}{3/2\zeta\Omega}/kT. \]

(5)

Here, \( \tau_{C0} \) is the yield stress at \( T = 0 \), while \( \tau_{CT} \) is at finite \( T \). One obtains

\[ \tau_{CT} = \tau_{C0} - \tau_{C0}[(k/\beta)\ln(\omega_0/C\dot{\gamma})(G_{0T}/G_{0Tg})]^{2/3}. \]

(6)

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\[ \tau_{CT} = \tau_{C0} - \tau_{C0}[(k/\beta)\ln(\omega_0/C\dot{\gamma})(G_{0T}/G_{0Tg})]^{2/3}. \]

(8)

where \( t = T/T_g \). The factor \( (G_{0T}/G_{0Tg}) \) incorporates the weak dependence of \( G \) on the thermal expansion of a fixed glass configuration. \( G_{0T} \) has been experimentally determined [15,18] to be a linear function of \( T \). For Vitreloy 1 [15], one finds \( dG_{0T}/dT \sim 4 \times 10^{-3} \) (GPa/K) with \( G_0 \sim 37 \) GPa at 0 K. Since the thermal expansion coefficient will drop at very low \( T \), one obtains an upper bound for the fractional change in \( G_{0T}/G_{0Tg} \) from 0 K to \( T_g \) as \( \Delta_{max} = (T_g/G_0)(dG_{0T}/dT) \sim 0.07. \) Similarly, we estimate \( \Delta_{max} \sim 0.11 \) for Pd40Ni30P20 [18]. The \( t \) dependence of \( (G_{0T}/G_{0Tg}) \) gives a maximum correction to the second term in Eq. (8) at \( t \sim 1 \) (near \( T_g \)) of order 5%–7%. The logarithmic term in Eq. (8) involves \( \omega_0 \) and is estimated to be the frequency of shear phonon of nm wavelength (\( \sim 10^{13} \) Hz). With typical strain rates (in yielding experiments) of \( 10^{-2} \sim 10^{-4} \) s\(^{-1} \), we have \( \ln(\omega_0/C\dot{\gamma}) \sim 30 \). An order of magnitude change in either \( \omega_0 \) or \( \dot{\gamma} \) changes the logarithmic term by \( \sim 5\% \). The dependence of \( \tau_{CT} \) on \( T \) is thus dominated by the \( r^{2/3} \) term.

The dotted curve in Fig. 2 was obtained using Eq. (8) (square bracket taken as a constant) to “fit” the dependence of \( \tau_{CT} \) at \( T_g \) (fixed \( T \)) and varying \( T_g \) for the 30 metallic glasses (open circles) and the \( t \) dependence of individual alloys (filled symbols). This fit gives \( \tau_y/G = \gamma_{C0} + \gamma CT m \) where \( \gamma_{C0} = 0.036 \pm 0.002, \gamma C = 0.16 \pm 0.002, \) and \( m = 0.62 \pm 0.2. \) Equation (8) explains both the \( T \) dependence of \( \tau_y \) for all individual amorphous alloys and the “\( T_g \) dependence” for 30 glasses at fixed \( T_g \) with an exponent “\( m \)” consistent (within error) with the predicted value “2/3.” The coefficients \( \gamma_C \) and \( \gamma C \) are approximately universal constants. The present classical model is expected to break down at very low \( T \). Low \( T \) data shown in the inset of Fig. 2 suggest “quantum effects” on yielding when shear phonon modes “freeze out” at very low \( T \).

For the CSM, the elastic response of an STZ is nonlinear as \( \tau \) increases from 0 to \( \tau_C \). The actual critical strain at \( \tau_C \) is not \( \tau_{CT}/G \) (as in experiments), but rather \( \pi \tau_{CT}/2G \) with the factor \( \pi/2 \) arising from nonlinear elasticity. The role of nonlinear elasticity and nonaffine atomic displacements in the shear response of an STZ has been recently discussed [35,36]. In both the Frenkel model and simulations [35], the compliance at finite stress, \( G_{\tau^{-1}} \), diverges at \( \tau_C \). Experimentally, one measures yield stress, not strain,
so the experimental $\gamma_C$ at yield underestimates the actual strain of the STZ. Further, the macroscopic material comprises a statistical distribution of STZ’s with distributed values of $G$ and $\tau_C$, varying with location and orientation. Yielding is expected when a critical fraction of unstable STZ’s results in global instability.

In conclusion, plastic yielding of metallic glasses at $T_R$ is roughly described by an average elastic shear limit criterion, $\tau_Y = \gamma_C G$, where $G$ is the shear modulus of the unstressed glass, and $\gamma_C = 0.0267 \pm 0.0020$. Closers analysis reveals that $\gamma_C$ depends on $t = T/T_g$. A CSM inspired by Frenkel’s work and recent molecular dynamics simulations is developed to explain these empirical findings. Yielding is treated as a fold catastrophe obeying a scaling law $W(\tau)/[G_{s}(\delta \gamma)^2] = R$. Applied on average, this scaling law leads to a “$t^{2/3}$ law,” $\tau_{CT}/G = \gamma_{C0} - \gamma_{C1}(t)^{2/3}$, for flow stress of metallic glasses where $\gamma_{C0}$ and $\gamma_{C1}$ are weakly material dependent. A fit to all experimental data yields $\gamma_{C0} = (0.036 \pm 0.002)$, $\gamma_{C1} = (0.016 \pm 0.002)$, and an exponent $m = 0.62 \pm 0.2$. A similar derivation of the “$T^{2/3}$ law” has appeared in the literature on yielding in crystals [37]. Gaunt also derived a similar law for thermally activated domain wall motion in disordered magnets [38]. To the extent that plastic yielding in nonmetallic glasses (oxides, molecular glasses, etc.) is a fold catastrophe, one might expect Eq. (8) to be valid more generally although $\gamma_{C0}$ may vary. The present CSM model may establish a basis for a broader understanding of glass physics.

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