The Role of Disorder and the Elastic Robustness of Bulk Metallic Glasses

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ABSTRACT

Despite significant atomic-scale heterogeneity, bulk metallic glasses well below their glass transition temperature exhibit a surprisingly robust elastic regime and a sharp elastic-to-plastic transition with a yield stress that depends approximately linearly on temperature. The present work attempts to understand these features within the framework of thermally activated plasticity. The presented statistical thermal activation model, in which the number of available structural transformations scales exponentially with system size, results in two distinct temperature regimes of deformation. At temperatures close to the glass transition temperature thermally activated Newtonian plastic flow emerges, whilst at lower temperatures the deformation properties fundamentally change due to the eventual kinetic freezing of the available structural transformations. In this regime, a linear temperature dependence emerges for the stress which characterises the elastic to plastic transition. For both regimes the transition to macroscopic plastic flow corresponds to a transition from a barrier energy dominated to a barrier entropy dominated statistics. The work concludes by discussing the possible influence that kinetic freezing might have on the low temperature heterogeneous and high temperature homogeneous plasticity of bulk metallic glasses.

INTRODUCTION

The deformation properties of bulk metallic glasses (BMGs) are broadly characterised by two temperature regimes [1]. In the high temperature regime, close to the glass transition temperature, BMGs deform homogeneously with the strain rate properties being reasonably well understood by thermally activated Newtonian plastic flow. At lower temperatures, plasticity becomes heterogeneous leading to low ductility in tension and shear banding in compression. In this regime of temperatures both athermal [2] and thermal [3] theories of plasticity have been proposed. Experimentally the yield stress has a decreasing, approximately linear, dependence on stress that is insensitive to material type when normalised with respect to a representative shear modulus and the glass transition temperature [3]. As the temperature approaches (and depending to the strain rate) passes, T_g, there is also an abrupt drop in the yield stress as the plasticity transits to the high temperature homogeneous deformation mode [4].

The present work outlines an attempt to understand the entire temperature range of plasticity via the thermal activation hypothesis and a distribution of relevant energy barriers. As with viscosity, a characteristic time scale of irreversible structural transformation activity is considered, τ_p, where below the glass transition temperature its inverse is seen as a plastic rate. Since in the low temperature regime, the elastic regime is robust and yield is a well defined and reproducible material property [5], studying the resulting temperature and stress dependence of $[\tau_\mathrm{p}]^{-1}$ can give insight into the transition from elasticity to plasticity. At higher temperatures, where the transition to plasticity is not so well defined, $[\tau_\mathrm{p}]^{-1}$ will give a more qualitative insight into the stress scale of the early stages of deformation.

THEORY

The reproducibility of the yield stress at low temperatures suggests BMG failure is an intrinsic property of the material [5] and at a large enough length scale BMGs may be considered structurally homogeneous. It is the calculation of $[\tau_{\mathrm{p}}]^{-1}$ at this length scale that is of current interest. For this length scale to be homogeneous, a sufficient amount of self-averaging must occur with respect to a shorter heterogeneous length scale. Thus

$$[\tau_{\mathrm{p}}]^{-1} = \sum_{n=1}^{N'} [\tau_{\mathrm{p0},n}]^{-1}(T), \tag{1}$$

where $[\tau_{\mathrm{p0},n}]^{-1}(T)$ is the particular plastic rate for the nth heterogeneous volume element and N' is the number of such heterogeneous volume elements leading to a well-converged self-averaged $[\tau_{\mathrm{p0}}]^{-1}(T)$. If the associated heterogeneity volume contains N atoms, then the homogeneous volume element contains $N' \times N$ atoms.

Under the assumption of thermally activated plasticity, the plastic rate associated with one particular heterogeneity volume may be written as a linear sum of the $M = M(N)$ thermally active transition rates available to that volume element:

$$[\tau_{\mathrm{p0,n}}]^{-1}(T) = \sum_{i=1}^{M} [\tau_{\mathrm{p0},ni}]^{-1}(T) \exp\left(-\frac{E_{\mathrm{p0},ni}}{k_{\mathrm{B}}T}\right), \tag{2}$$

where $[\tau_{\mathrm{p0},ni}]^{-1}(T)$ and $E_{\mathrm{p0},ni}$ are the attempt rate and barrier energy for the ith irreversible structural transformation within the nth heterogeneous volume element.

In terms of the underlying potential energy landscape (PEL), the simple (first order) expression of eqn. 2 is only valid for thermally activated processes that do not multiply recross their energy barrier. This naturally leads to a coarse graining of the PEL, in which the barriers and (now diffusive) prefactors entering into eqn. 2 underly the collective microscopic activity that results in a lasting escape from a characteristic energy valley. By analogy to the under cooled liquid PEL framework [6, 7] where two distinct time scales occur — the "slow" α-relaxation and "fast" microscopic β-relaxation modes — the self-averaging of eqn. 1 into which eqn. 2 has been subsituted, is found to reduce to

$$[\tau_{\mathrm{p0}}]^{-1} = [\tau_{\mathrm{p00}}]^{-1} \exp\left(-\frac{E_{\mathrm{p00}}}{k_{\mathrm{B}}T}\right) M \left\langle \exp\left(-\frac{E_{\mathrm{p0}}}{k_{\mathrm{B}}T}\right) \right\rangle. \tag{3}$$

Eqn. 3 consists of a diffusive attempt rate with a simple Arrhenius temperature dependence, representing the mediating β mode relaxation dynamics, and a thermal factor whose temperature dependence will be derived from the statistical properties of the α-relaxation mode coarse grained PEL [8]. Identifying, the relevant energy barriers with those of the α-relaxation mode barrier energy landscape is motivated by the known high temperature thermally activated homogeneous Newtonian plastic flow regime of BMGs, in which the corresponding activation energy (derived from strain rate sensitivity experiments) correlates strongly with the characteristic α-mode energy barrier derived from the fragility measurements at T_{g} for a wide range of BMGs [9].

The remaining average in eqn. 3 may be performed via an integration over a distribution of α-relaxation mode barrier energies:

$$M \left\langle \exp\left(-\frac{E}{k_{\mathrm{B}}T}\right) \right\rangle = M \int_0^{\infty} dE\, P(E) \exp\left(-\frac{E}{k_{\mathrm{B}}T}\right), \tag{4}$$

where the form of $P(E)$ is motivated by the relation between M and N.

For the number of minima in a glassy PEL, Stillinger developed the concept of inherent structures (the associated atomic configurations) whose number was found to scale exponentially with atom number [10]. This relation can also be extended to the case of the total number of stationary points [11, 12]. Thus, presently, $M = \exp(\overline{\alpha}N)$ where $\overline{\alpha}$ can be viewed as a bulk material parameter, the saddle-point enumeration number characterising the total number of available structural transformations per atom. Such a form has also been assumed in early thermodynamical models of viscosity [13, 14]. As with the energy dependence of the number of inherent structures [15], the barrier energy dependence of $\overline{\alpha}$ (the saddle-point enumeration function) has been found to be a quadratic function [11] suggesting that the appropriate starting point for $P(E)$ for a finite N, is a Gaussian distribution with an extensive mean $\overline{E}N$ and an extensive standard deviation squared $(\delta E)^2 = \left(\delta\overline{E}\sqrt{N}\right)^2$.

For a Gaussian, the integral in eqn. 4 can be evaluated, giving

$$M \left\langle \exp\left(-\frac{E}{k_{\mathrm{B}}T}\right) \right\rangle \approx \exp\left(N \left[\overline{\alpha} - \frac{\overline{E}}{k_{\mathrm{B}}T} + \frac{1}{2}\left(\frac{\delta\overline{E}}{k_{\mathrm{B}}T}\right)^2 \right] \right). \tag{5}$$

For a sufficiently large value of N, the above (and also $[\tau_{\mathrm{p}}]^{-1}$ via eqn. 3) will have a negligible value if the factor within the argument of the exponential is negative and a large value when it is positive. Assuming $\overline{E}$, $\delta\overline{E}$ and $\overline{\alpha}$ are fixed material parameters, the critical temperature at which this occurs is

$$T_{\mathrm{c}} = \frac{\overline{E}}{k_{\mathrm{B}}} \frac{\left(\delta\overline{E}/\overline{E}\right)^2}{1 - \sqrt{1 - 2\left(\delta\overline{E}/\overline{E}\right)^2 \overline{\alpha}}}. \tag{6}$$

The critical temperature is thus independent of N and therefore the size of the heterogeneous volume element. For $T < T_{\mathrm{c}}$, eqns. 5 and 3 become negligible, whereas for $T > T_{\mathrm{c}}$ they becomes exponentially large. Thus T_{c} defines the temperature at which there is a fundamental change in the degree of plasticity and will be referred to as the plastic transition temperature. The sharpness of this transition is determined by the value of N.

What is the nature of this transition? Eqn. 5 can be written as

$$M \left\langle \exp\left(-\frac{E}{k_{\mathrm{B}}T}\right) \right\rangle = \exp\left(-\frac{N\overline{E}_{\mathrm{app}}(T)}{k_{\mathrm{B}}T}\right) \times \exp\left(N \left[\overline{\alpha} - \frac{1}{2}\left(\frac{\delta\overline{E}}{k_{\mathrm{B}}T}\right)^2 \right] \right), \tag{7}$$

where the apparent barrier energy, $\overline{E}_{\mathrm{app}}(T) = \overline{E} - \delta\overline{E}^2/(k_{\mathrm{B}}T)$, is the first moment of the distribution proportional to $P(E)\exp(E/k_{\mathrm{B}}T)$. The second term in eqn. 7 is interpreted as the apparent number of available structural transformations. At temperatures, $T < T_{\mathrm{c}}$, the smallness of the thermal factor involving $\overline{E}_{\mathrm{app}}(T)$ dominates and eqn. 5 becomes negligible, whereas at temperatures, $T > T_{\mathrm{c}}$, the exponential largeness of the apparent number of available structural transformations dominates and eqn. 7 becomes non-negligible. The transition temperature, T_{c}, is defined when both these terms are comparable. Since the left hand side of eqn. 5 has the mathematical structure of an average partition function, an analogy to thermodynamics can be made allowing the argument of the exponential in eqn. 5 to be interpreted as a free *barrier* energy, and thus T_{c} as the temperature at which the barrier statistics changes from an internal *barrier* energy to a entropy *barrier* dominated regime [16].

Is eqn. 7 always valid? Upon sufficient decrease of temperature, the argument of the last term in eqn. 7, will become zero resulting in the apparent number of available structural transformations
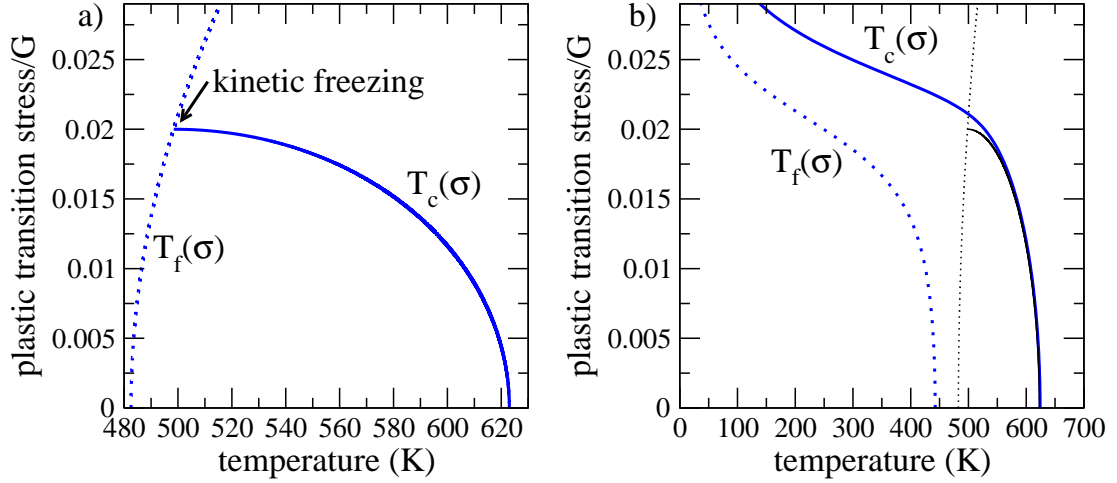
Figure 1: a) Dependence of plastic transition and freezing temperature on applied load for a) a Gaussian and b) a modified Gaussian with which gives a zero probability at zero barrier energy. Model parameters are derived from the material properties of Viteroly-1.

equalling one. This occurs at temperature $T_f = \delta\overline{E}/\sqrt{2\overline{\alpha}}$ and therefore at an apparent barrier energy $\overline{E}_{app}(T_f) = \overline{E} - \sqrt{2\overline{\alpha}}\delta\overline{E}$. Below this temperature, eqn. 5 is no longer applicable with the barrier statistics fundamentally changing to that of the extreme value centred around $\overline{E}_{app}(T_f)$. In the thermodynamic analogy, the system "freezes" into one characteristic available barrier energy [16]. Freezing is a phenomenon that occurs in spin-glasses and was first derived for the so-called random energy model of Derrida [17] and is intimately connected to extreme value statistics and the replica symmetry breaking method for use in quenched averages [18]. For $T < T_f$, eqn. 5 becomes a constant equal to $\exp\left(-\overline{E}_{app}(T_f)/\left(k_B T_f\right)\right)$. This has important consequences upon the application of a load and will be referred to as kinetic freezing.

RESULTS

The application of an external stress will affect the distribution of barrier energies via a change in its first and second moments, $\overline{E}$ and/or $\delta\overline{E}$. Since the application of an external load strongly breaks the symmetry of the system, it is assumed that the energy barriers will with equal probability either increase or decrease, broadening $P(E)$. To leading order this will be represented as $\delta\overline{E}(\sigma) = \overline{E}(0)\left(1 + (\sigma/\sigma_0)^2\right)$ where (presently) σ is a simple shear. This will result in stress dependent plastic transition $T_c(\sigma)$ and freezing $T_f(\sigma)$ temperatures.

Fig. 1a displays the resulting plastic transition and freezing temperatures as a function of σ for a choice of parameters $\overline{E}$, $\delta\overline{E}$, N and σ_0. Inspection of this figure reveals that in the vicinity of $T_c(0)$, the stress required for the plastic transition to occur rapidly increases upon lowering the temperature, eventually saturating to a value at which freezing occurs: $T_c(\sigma_f) = T_f(\sigma_f)$. At this freezing stress/temperature, $\overline{E}_{app}(T_f) = 0$, and eqn. 7 equals unity resulting in a stress independent plastic rate and the inapplicability of the Gaussian model for temperatures less than T_f. This is an artifact of the Gaussian distribution which does not limit to zero at zero barrier energy.

The parameters $\overline{E}$, $\delta\overline{E}$, N used in fig. 1 may be uniquely determined as a function of $\overline{\alpha}$ by recognising 1) at zero-load, the plastic transition, T_c, will be in the vicinity of the glass transition temperature and the apparent barrier energy at this temperature is related to the kinetic fragility,

and 2) the emergence of kinetic freezing will correspond to the onset of a distinct low temperature deformation regime. The parameter σ_0 can be chosen independently and sets the scale of the load axis. In fig. 1 it chosen so that at kinetic freezing, the stress is equal to $0.02G$ where G is some representative shear modulus. The parameter values used in fig. 1 are those for Viteroly-1 [1, 9]. When doing this, such curves become independent of $\overline{\alpha}$.

To modify the Gaussian distribution in a way that has the correct limit $P(E \to 0) \to 0$, the argument within the exponential is changed from $(E - N\overline{E})/\delta\overline{E}$ to $(g(E) - N\overline{E})\delta\overline{E}$, where presently $g(E) = E - (aN)^2/E$ — a form which ensures an extensive apparent barrier energy. Thus an additional parameter, a, is required. Such a modification still facilitates an analytical solution to the integral of eqn. 4. Fig. 1b displays the resulting critical and freezing temperatures as a function of applied load using the same parameters as in fig. 1a, revealing the avoidance of kinetic freezing and a distinct low temperature deformation regime that is approximately linear. The value of a sets the gradient of this linear regime where decreasing its value limits to plateau at σ_f. At very low temperatures the plastic transition stress rapidly increases eventually diverging at vanishingly small temperatures — the athermal limit where the thermal activation hypothesis central to the present model breaks down.

DISCUSSION AND CONCLUDING REMARKS

Thus far, only the temperature dependence of eqn. 4 has been taken into account when determining the plastic transition temperature T_c. The actual plastic rate, given in eqn. 3, has a prefactor with the parameters $[\tau_{p00}]^{-1}$ and E_{p00} which characterise the underlying microscopic (β-mode) structural transformations that mediate the α-relaxation processes. Moreover, for application to a deformation at a particular strain rate, the plastic transition criterion developed from eqn. 5 must be replaced with the condition $\tau_{exp} \times [\tau_p]^{-1}(T_c) \simeq 1$, that is, when the plastic rate is comparable to the experimental timescale τ_{exp} ($\propto 1/\dot{\varepsilon}^2$) of the deformation experiment. It is straight forward to show that these three additional parameters affect the plastic transition temperature, T_c via the simple renormalisation: $\overline{E} \to \overline{E} + E_{p00}/N$ and $\overline{\alpha} \to \overline{\alpha} + \ln(\tau_{exp}/\tau_{p00})/N$. Because of the logarithmic dependence on τ_{Exp}/τ_{p00}, the values of $[\tau_{p00}]^{-1}$ and τ_{exp} need only be known to order of magnitude accuracy.

The derived stress versus transition temperature reproduces well the experimentally observed universal behaviour of yield/peak flow stress versus temperature at low temperature and also the rapid drop in peak flow stress seen in the vicinity of T_g [1, 3, 9, 4]. That the curves in fig. 1 are independent of $\overline{\alpha}$ suggests an insensitivity of yield to the local atomic structure characterized by $\overline{\alpha}$, a possible origin of the experimentally observed universal behaviour at low temperature. For the BMG, Viteroly-1, N can be typically several thousands of atoms corresponding to a heterogeneous length scale in the nano-meter regime, and in part, to a sharp transition from elastic to plastic deformation behaviour.

Kinetic freezing corresponds to a statistics in which many heterogeneous volumes cannot deform at the average rate, suggesting a fundamental origin to low temperature heterogeneous plasticity. Although kinetic freezing does not explicitly occur at the plastic transition temperature when the modified Gaussian is used, the proximity of the freezing temperature to the plastic transition temperature at low temperatures might still have an influence on the barrier statistics. At higher temperatures, far from the kinetic freezing regime, the statistics is more homogeneous with all heterogeneous volume able to deform via the apparent barrier energy at that temperature, leading to a correspondingly homogeneous plasticity.

In conclusion, a thermal activation hypothesis in conjunction with an exponentially large number of available structural transformations, whose energy barriers follow a distribution with extensive first and second moments, has been used to investigate the characteristic plastic rate of BMGs. It is found that there exist two temperature regimes of deformation: 1) a high-temperature regime where the stress at which significant plastic activity occurs, rapidly rises with reducing temperature and an exponentially large number of structural transformation are available for plastic deformation to occur and 2) an approximately linear regime of stress versus plastic transition temperature in which the available number of thermally accessible structural transformations has drastically reduced. This latter regime is found to be intimately connected to the phenomenon of kinetic freezing in which the statistics of extremal values centred on a single dominant barrier energy scale controls those structural transformations that are thermally accessible.

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