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Evaluation of approximate measurements of activation-free-energy spectra of shear transformation zones in metallic glasses

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ABSTRACT

For many years, the only experimental activation free energy spectrum for shear transformations in metallic glasses had been obtained by quenching from high temperature during creep, followed by temperature stepping (Argon and Kuo, 1980). We show that the approximation associated with attributing a single activation energy to each temperature leads to an artificial drop in the spectrum at high activation energies. The detailed spectra of potential shear transformation zones we have recently obtained, which exhibit an atomically quantized hierarchy and are monotonic, lead to the same spectrum shape as obtained by Argon and Kuo when the approximation inherent to the temperature stepping method is applied.

1. Introduction

The temperature dependence of thermally-activated processes provides important insights into the underlying microscopic processes. Arrhenius behavior of a macroscopically-measured process provides an apparent activation energy that is typically indicative of a microscopic process. In a glass, however, there is often a distribution of activation energies for atomic transport. The inverse problem of computing a spectrum from experimental data is challenging since the spectrum is only given by an implicit equation. In a pioneering study, Argon and Kuo [1] determined the spectra of activation free energies for shear transformations in several metallic glasses. Their method consisted of (a) subjecting a sample to torsional creep at high temperature; (b) quenching it under stress; (c) stepping the temperature up and holding it until the anelastic strain recovery rate decreased significantly; (d) repeating at a set of temperatures T_j and corresponding times t_j, measuring the amount of strain recovery at each. This quantity was a measure of the number of shear transformations that took place at that temperature. The dominant activation free energy at T_j was estimated as

$$\Delta F_j = -k \frac{\partial \ln \dot{\gamma}}{\partial (1/T)}\bigg|_{T_j} \quad (1)$$

where $\dot{\gamma}$ is the shear strain rate and k is Boltzmann's constant. The spectra obtained increased monotonically with free energy, then exhibited a drop at the highest free-energy value. It is obvious that the temperature-stepping method is limited by its approximations. The processes that take place at each temperature have a range of barrier heights and not a single value. In addition, there is a practical limitation associated with the thermal inertia and the corresponding temperature stabilization time after each step.

We have recently obtained the size–density distribution of potential shear transformation zones by monitoring quasi-static anelastic recovery in an Al-based metallic glass [2]. From the data, we computed the spectrum of relaxation times, which exhibited distinct peaks. Each of these peaks was attributed to a Voigt unit [3] in series with the others (Fig. 1), representing one class of shear transformation zones (STZs). While there are equivalent arrangements of springs and dashpots that describe the same overall behavior, the arrangement we used can be related in the most straightforward way to the number density of each STZ class, since each class contributes additively to the strain. Using Argon and Shi's analysis [4], based on the Eshelby model [5], we concluded each spectrum peak corresponded to STZs comprising a specific number of atoms, ranging from 14 to 21. Smaller STZs were rare and too fast to be detected, and larger potential STZs, while abundant, were kinetically frozen at the temperature of the experiment. The model was further verified by analyzing frequency-dependent loss-modulus data obtained at different temperatures [6] and obtaining an Arrhenius plot for each STZ size in the range 25–33 atoms. While Ref. [1] suggested that the width of the spectrum

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reflected a distribution of free volume, our results indicated that the width was due to the range of STZ sizes. Since the activation free energy is proportional to the STZ volume [4], the size–density distribution yields the spectrum of activation free energies for shear transformations. The spectra we obtained are strictly monotonic and do not exhibit a drop at the high end. In this paper, in order to compare these results with Ref. [1], we predict spectra obtained by the temperature-stepping method by applying its approximations to the detailed data of Ref. [2]. We show that the same qualitative spectrum shape is obtained.

2. Results and discussion

The purpose of this paper is to illustrate qualitatively the systematic error associated with the temperature-stepping method. Since a finite number of STZ sizes affect the anelastic relaxation at a given temperature, we approximate for simplicity and without loss of generality the qualitative shape of the spectrum obtained in Refs. [2,7] with five STZ sizes ($N = 5$ in Fig. 1). Each STZ size is represented in Fig. 1 with a Voigt unit – a spring with effective modulus E_i in parallel with a dashpot with effective viscosity η_i, $i = 1,\ldots,5$. Both E_i and η_i are inversely proportional to the number density of STZs of the respective size. The corresponding activation free energy values are set to $\Delta F_i = 1.00$–1.20 eV, in steps of 0.05 eV. The corresponding volume fractions c_i, $i = 1,\ldots,5$, are selected to qualitatively resemble our experimental results [2,7] (Fig. 2). We note that the qualitative conclusions presented below are not affected by these specific choices.

The time constant associated with process i is equal to $\tau_i = 3\eta_i/E_i$. Based on Refs. [2,4], it is given by:

$$\tau_i(T) = \frac{3\,kT}{2\,\mu\,(1+\nu)\,\nu_G\,\gamma_0^C\,\gamma_0^T\,\Omega_n}\exp\left[\frac{\Delta F_i}{kT}\right] \tag{2}$$

at temperature T, where ΔF_i is proportional to the STZ volume, Ω_n, with $n = n_0 + i$, $i = 1,\ldots,5$, being the number of atoms the STZ comprises and $n_0 = 19$ selected for the present example. ν is Poisson's ratio, μ, the shear modulus and ν_G is the attempt frequency. γ_0^T is the transformation shear strain and γ_0^C its value when constrained by the elastic matrix surrounding the STZ. Below the glass transition temperature, variation of μ with temperature is small and will be neglected.

In our simulation of the temperature-stepping method, it is assumed that the sample is quenched to 0 °C, at which all processes are frozen. The temperature is then stepped to $T_j = 20$, 40, 60, 80 and 100 °C ($j = 1,\ldots,5$). Values of $\tau_i(T_j)$ i, $j = 1,\ldots,5$, (Eq. (2)) are displayed in Fig. 3 for each temperature. In the simulation, anelastic relaxation at each temperature T_j is allowed to take place for a duration of $2\tau_j(T_j)$. This allows for 86% strain recovery for the corresponding STZ size Ω_{n_0+j}, while maintaining $2\tau_j(T_j) < \tau_{j+1}T_j$. The contribution of all five processes is taken into account at each temperature. The strain recovery curves are shown in Fig. 4. Simulated c_i values as a function of approximate ΔF_i (Eq. (1)), both according to Ref. [1], are shown in Fig. 5. These are compared with the assumed input values. In the simulation, ΔF_i values are shifted downward, and c_i drops significantly at the highest ΔF_i. These trends are due to the fact that at low temperature, because it neglects the contribution of high-ΔF_i STZs, the temperature-stepping method attributes all the recovery to lower ΔF_i and thus overestimates c_i for small i. By the time the highest temperature is reached, many of the STZs corresponding to $i = 5$ have already relaxed, leading to an underestimate of c_5.

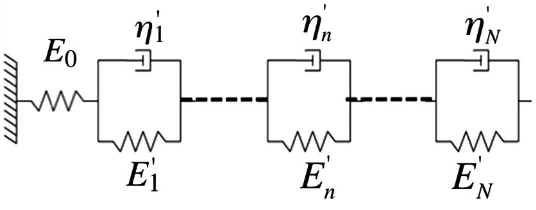

Fig. 1. The metallic glass is modeled as a set of N Voigt units in series, each consisting of a spring (effective modulus E_i) and dashpot (effective viscosity η_i), $i = 1,\ldots,N$.

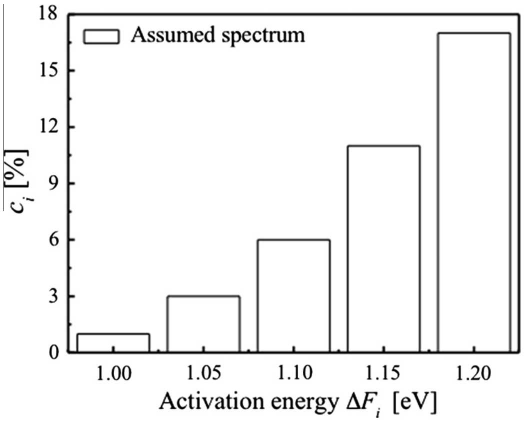

Fig. 2. Assumed spectrum of activation free energies, selected to resemble the experimental results of Refs. [2,7].

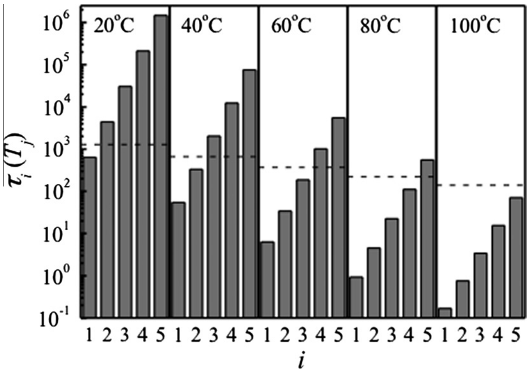

Fig. 3. Time constants corresponding to STZs of type i at temperatures T_j, i, $j = 1,\ldots,5$. The broken line denotes $2 \times \tau_j(T_j)$, the simulated hold time at each temperature T_j, which is always smaller than $\tau_{j+1}(T_j)$.

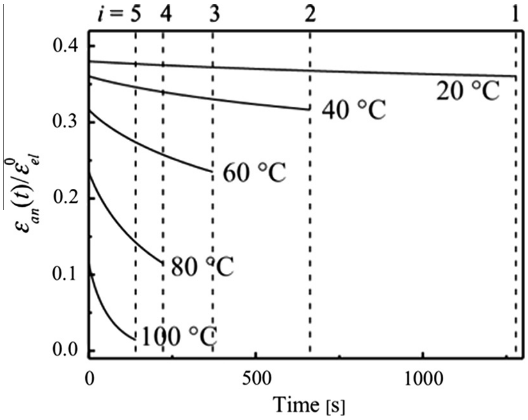

Fig. 4. Simulated anelastic strain recovery during temperature stepping at T_j, $j = 1,\ldots,5$. The corresponding hold times, $2 \times \tau_j(T_j)$, are indicated with broken lines.

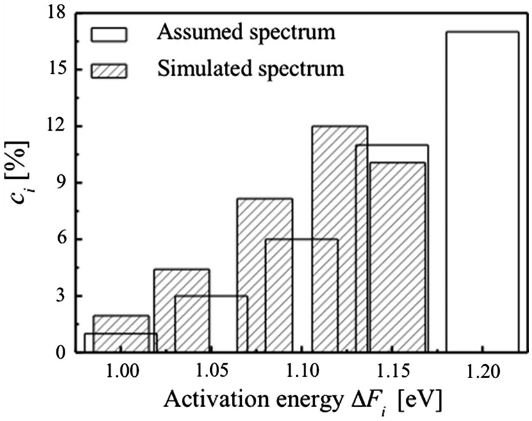

Fig. 5. Assumed spectrum compared with that obtained using the temperature-stepping approximation. Both the activation energy values and spectrum shape are affected. The latter is similar to those in Ref. [1].

For the case of activated flow state, when potential STZs are continually created and annihilated, Bouchbinder and Langer [8] postulated a distribution of ΔF proportional to $\exp(b\Delta F/\chi)$, where b is a dimensionless constant and χ is the effective disorder temperature in energy units. They also reasonably argued that the only shear transformations that contribute to flow are those that take place at rates higher than the rate of creation/annihilation of potential STZs. Consequently, they introduced a (smoothed) cutoff at an upper limit on ΔF, and pointed out that the resemblance of the resulting distribution to those in Ref. [1]. At sufficiently low stress and temperature, such as in Ref. [1] and in our work, the distribution of potential STZs is fixed. For this regime, we emphasize the need to distinguish between the fundamental spectrum and kinetic effects on the observable spectrum. The fundamental spectrum may have an upper limit due to pinning points or sample size. This ultimate limit is generally higher than the kinetic limit: as we mention above, the observed range of ΔF values is a window in a broader hierarchy. In Ref. [2], we observed the spectrum of STZs consisting of 14–21 atoms. c_{21} had to be corrected for the fact that 21-atom STZs had not reached mechanical equilibrium under prior constraint. In later work [7], using longer constraining times, we also observed the contribution of 22-atom STZs to the spectrum. While it is possible that the drop in the spectrum at the highest ΔF in Ref. [1] was influenced by the potential STZs corresponding to this value not equilibrating during prior creep, the present work shows a clear artifact contributing to the observed drop. In a separate publication [7], we present an expression for the spectrum, based on free-volume statistics.

3. Summary

In quasi-static anelastic relaxation experiments, the activation-free-energy spectra for shear transformations are monotonically increasing. An artifact of the temperature-stepping method likely dominates the observed drop at high ΔF values.

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