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A comprehensive atomistic analysis of the experimental dynamic-mechanical response of a metallic glass

J.D. Ju [a], M. Atzmon [a,b,*]

[a] Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, MI 48109, USA
[b] Department of Nuclear Engineering and Radiological Sciences, The University of Michigan, Ann Arbor, MI 48109, USA

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Abstract

It is shown that assumed anelastic relaxation-time spectra can be recovered reliably from simulated loss–modulus curves that include noise by nonlinear least-squares fitting. The same method is used to obtain spectra for published experimental data on a metallic glass. The results provide a comprehensive kinetic picture of the atomically quantized hierarchy of shear transformation zones (STZs). We resolve a window of STZs consisting of 25–33 atoms, and a simultaneous fit yields the Arrhenius behavior for each size. The corresponding activation energies are 1.75–2.31 eV. The high activation energy that is often observed above T_g is shown to be an artifact of the temperature dependence of the high-frequency shear modulus. The hierarchy of STZ sizes is consistent with both α and β relaxations, suggesting that they originate from the same microscopic mechanism.

Keywords: Metallic glasses; Internal friction; Dynamic phenomena; Shear transformations; Constitutive equations

1. Introduction

A glassy structure can exist in many materials classes, e.g. metals, polymers, ceramics and semiconductors. Because they lack long-range order, glasses have long posed challenges to scientists. Their static structure is still a subject of active experimental and computational research. Their response to a time-varying field, e.g. electromagnetic or mechanical, is an important probe of their physical behavior, as it allows for experiments that span a wide range of time constants.

The loss modulus, i.e. the imaginary part of the dynamic elastic modulus, is a probe of the degree of dissipation in a material [1]. For a single process with relaxation time constant τ, the loss modulus is a Cauchy function of the angular frequency of the applied force, ω, and peaks at $1/\tau$. However, it is generally observed to be a broader function of ω than a Cauchy function. It has been assumed that relaxation-time spectra cannot be obtained directly from measured loss moduli (or dielectric response), primarily because of the intrinsic width of the Cauchy function. Therefore, a stretched exponent, $\exp(-(t/\tau)^{\beta})$ [2–4], where τ and β are constants, or other functions are often used as empirical descriptions of the time-dependent relaxation [5,6], which amounts to an a priori assumption about the shape of the relaxation-time spectrum. A tail observed at high frequencies and fixed temperature, or at low temperatures and fixed frequency, has been attributed to relaxation processes that differ qualitatively from those responsible for the main part of the peak [7–11]. While molecular dynamics simulations have been employed to describe the dynamic response of a glass [11–13], caution should be exercised in their interpretation, since they have to be

* Corresponding author. Address: The University of Michigan, Cooley Bldg., 2355 Bonisteel Blvd., Ann Arbor, MI 48109-2104, USA. Tel.: +1 734 764 6888; fax: +1 734 763 4540.
E-mail address: atzmon@umich.edu (M. Atzmon).

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conducted at strain rates and stresses that are far higher than in conventional experiments, at which the deformation mechanism may differ [14]. A comprehensive microscopic model that can be compared to experimental results in quantitative detail is lacking.

Based on observations in 2-D [15] and 3-D [16] physical analogues, viscoelastic deformation of metallic glasses has been modeled in terms of shear transformations [14,17]. In the low-stress regime, a shear transformation zone (STZ) [18] is an equiaxed atomic cluster that undergoes irreversible shear, while its surroundings deform elastically. We have recently obtained [19] anelastic relaxation-time spectra directly from quasi-static anelastic relaxation measurements in amorphous $Al_{86.8}Ni_{3.7}Y_{9.5}$ (at.%) without making any a priori assumption on the shape of the spectra. These exhibited peaks, manifesting an atomically quantized hierarchy of STZs. The size-density distribution of *potential* STZs was obtained from the data, and is consistent with our theoretical model [20]. In the present work, we use a similar approach to analyze the dynamic behavior of a metallic glass. We first generalize a method of direct spectrum analysis (DSA) [21], a nonlinear least-squares fitting method developed to obtain relaxation-time spectra from quasi-static anelastic data. We demonstrate that this method can reliably recover assumed spectra from simulated dynamic data that include noise, then apply the method to published data [22]. The temperature-dependent spectra we obtain resolve STZs by the number of atoms they comprise. The simultaneous fits we perform exhibit Arrhenius behavior for each STZ size, from 25 to 33 atoms, and yield the corresponding activation energies. The value of the transformation shear strain, 0.15, is obtained independently. Commonly observed phenomena are explained quantitatively by the present analysis.

2. Data analysis methodology

In order to validate the generalization of DSA [21] to dynamic data, we created simulated data sets, using assumed relaxation-time spectra, $f^a(\tau)$, consisting of several Gaussian peaks. An example is shown in Fig. 1(a), in which the spacing between the peaks is chosen to be irregular in the interest of generality. Also shown in Fig. 1(a) is the corresponding simulated loss modulus obtained by numerical integration,

$$E_s'' = E_0 \times \int f^a(\tau)\frac{\omega\tau}{1+\omega^2\tau^2} d\ln\omega \tag{1}$$

where E_0 is the high-frequency modulus. Normally distributed random noise with a standard deviation of 2×10^{-3} was added. To mimic typical experimental conditions, the E_s'' curves were truncated to the range $\omega_{min} = 1\times10^{-3}$ to $\omega_{max} = 9\ s^{-1}$ prior to their analysis. Because of the intrinsic width of the Cauchy function, these data contain spectrum information for reciprocal relaxation times that extend beyond this range.

DSA was subsequently performed by least-squares fitting the simulated data using the primal-dual interior-point filter line search algorithm, which allows the handling of problems with large numbers of inequality constraints [23]. The software package AMPL [24] was used with a nonlinear solver IPOPT [23]. The digitized data set for each temperature was fitted with the expression

$$E''(\omega) = \sum_{i=1}^{N} f_i \frac{\omega\tau_i}{1+(\omega\tau_i)^2} \tag{2}$$

with the f_i being fitting parameters, $N = 70$ and all τ_i fixed and logarithmically spaced, $\ln(\tau_i/\tau_{i-1}) = \Delta\ln(\tau)$. The corresponding spectrum is given by

$$f(\tau_i) = f_i/(E_0\times\Delta\ln\tau) \tag{3}$$

As an initial guess, all f_i were set equal to 0.01, and it was verified that the fitting results were independent of this choice. The analysis presented below was conducted for the τ range of $\tau_{min} = (\omega_{max})^{-1}/4$ to $\tau_{max} = 4(\omega_{min})^{-1}$, which provided the most comprehensive results.

Fits were performed with different prescribed tolerance targets, such that:

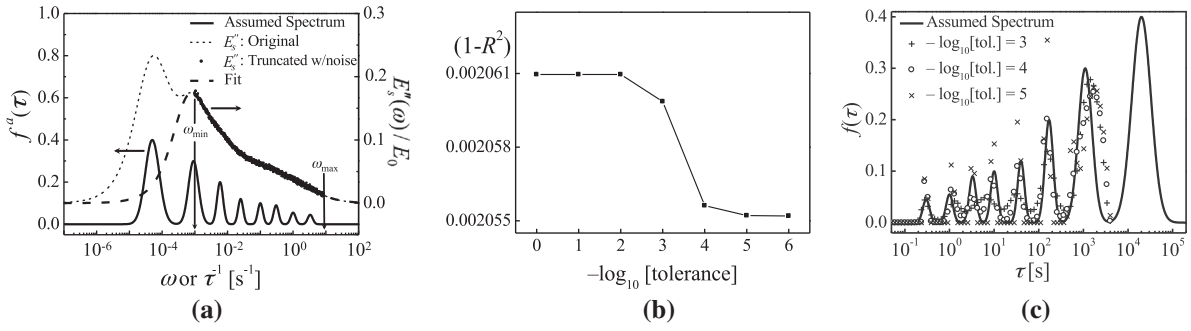

Fig. 1. (a) Assumed relaxation-time spectrum, $f^a(\tau)$, and corresponding simulated loss modulus, $E_s''(\omega)/E_0$, with noise included. The DSA fit to the truncated data is also shown. (b) $1 - R^2$ for DSA fits as a function of the prescribed tolerance for the simulated loss modulus of (a). A similar curve was created to determine the best fit for each experimental $E''(\omega)$ curve. (c) Assumed spectrum (same as in Fig. 1(a)) with fitting results obtained from the simulated data for three tolerance values. The tolerance value of 10^{-4}, at which $1 - R^2$ drops precipitously (Fig. 1(b)), yields the best fit.