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The atomistic mechanism of fast relaxation processes in $Cu_{65}Zr_{35}$ glass

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ABSTRACT

Molecular-dynamics simulations of the glass $Cu_{65}Zr_{35}$ show a rattling mode of atomic motion. While the frequency of the rattling mechanism is essentially independent of temperature and of the strain applied to the glass, the fraction of atoms undergoing rattling is dependent on temperature and strain. It is argued that the rattling motions constitute the 'fast processes' that lie between β relaxation and the boson peak in the characteristic spectrum of dynamic modes in glasses. It is concluded that the fast processes are a precursor to β relaxation and that their inhomogeneous distribution in the metallic glass is the origin of the shear transformation zones governing the onset of plastic flow.

1. Introduction

Recent years have seen intense interest in fast dynamic processes in supercooled liquids and glasses [1,2]. For electrically insulating glasses, dielectric spectroscopy reveals a range of phenomena, intrinsic to the glassy state, spread over a wide range of frequencies (Fig. 1). The α relaxation (10^{-6}–1 Hz) is associated with the glass transition; the β or Johari-Goldstein relaxation (10^{-2}–10^{7} Hz) is associated with modes in loosely packed regions; the boson peak (10^{12} Hz) is associated with an excess in the low-temperature vibrational density of states; and infra-red bands are found at even higher frequency [1–3]. Lunkenheimer et al. [1] found that there are significant dynamic modes between the β relaxation and the boson peak; in their comprehensive review of glass dynamics, they considered that the discovery of these intermediate *fast processes* (10^{8}–10^{11} Hz) was "the most important outcome" of their extended dielectric investigations.

In the present paper, we study such *fast processes* in a metallic glass. It is now understood that β relaxation in metallic glasses is closely related to deformation mechanisms, the glass transition, atomic diffusion and the breakdown in the Stokes-Einstein relation, and to crystallization [2,4,5]. The fast processes have particular importance because they may be the threshold to β relaxation. In particular, the fast processes may be critical in understanding the onset of plasticity in metallic glasses, and the link between that onset and structural inhomogeneity [6]. The fast processes are stronger relative to the boson peak for glasses formed from more fragile liquids [7]. Taking the intermediate-to-high fragility of metallic glass-forming liquids into account, fast processes may therefore be significant for metallic glasses. Understanding these processes and the onset of β relaxation may assist in the design of glasses to optimize properties.

Dielectric spectroscopy is not applicable to metallic glasses, which have been investigated using techniques such as dynamic mechanical analysis (DMA), in which characteristic dynamic modes are revealed by peaks in the loss modulus as a function of temperature. There is an α-relaxation peak, and β relaxation is indicated by anything from an excess wing on the α peak, to a shoulder, to a distinct β peak [5,8–10]. Recent studies have also found a second fast β′ peak [11,12] and a near-constant-loss mode [13] on the low-temperature side of the β peak. The shifts of loss peaks to higher temperature at higher frequency give the effective activation energy of the modes. For β relaxation in metallic glasses, the activation energy is 26 (±2)RT_g [2,5]; for the fast β' and near-constant-loss modes, it is roughly half this value [11–13]. In the context of the present work, we note that binary Cu-Zr glasses exhibit β relaxation as a shoulder on the α peak [9].

DMA has a limited frequency range, and is incapable of revealing

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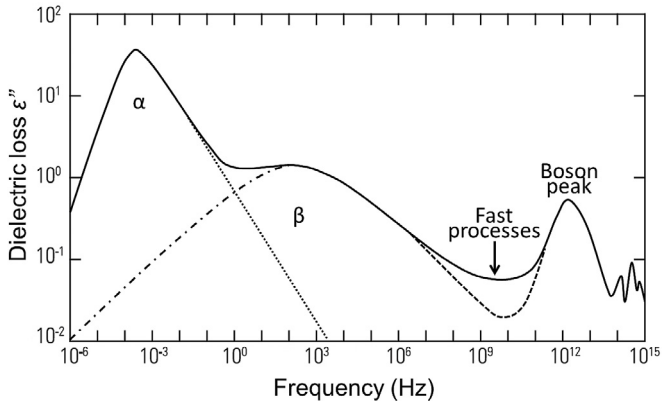

Fig. 1. Schematic spectrum of frequency-dependent dielectric loss in glass-forming systems, showing characteristic dynamic modes, in particular α and β relaxation. Reproduced with permission from Lunkenheimer and Loidl, Chem. Phys. 284 (2002) 205–219. Copyright 2015 Elsevier Science B.V.

the boson peak. This has, however, been detected in measurements of low-temperature specific heat of CuZr-based metallic glasses [14], and the boson peak and β relaxation are similarly affected by changes in metallic-glass composition [15]. In the absence of direct high-frequency spectroscopy measurements, molecular dynamics (MD) has proved to be a useful tool in elucidating structural and dynamic aspects of the boson peak. Jakse et al. [16] used MD to simulate a $Cu_{50}Zr_{50}$ (at.%) glass and found a well-defined peak consistent with the specific-heat measurements [14]. They found that the boson peak is associated with the "rattling" of both species of atoms in localized regions of relatively low density and defective structure. The participating atoms vibrate with mean-square amplitudes that are abnormally large and also span a wide range, reflecting the diversity of local coordinations. For the boson peak similarly found in MD simulations of a $Cu_{64}Zr_{36}$ glass, Ding et al. [17] focused on the 1% of vibrational modes of lowest frequency. These *soft modes* lie in the region of interest for the fast processes in Fig. 1, but the time dependence of atomic positions was not reported.

In the present work, our MD simulations of a similar Cu-Zr glass reveal additional modes that we identify with the fast processes described by Lunkenheimer et al. [1]. In contrast to the main relaxation peaks in Fig. 1, the boson peak is temperature-independent. The fast processes therefore sit in an interesting region between vibration (boson) and relaxation (β and β′) behavior [1,18].

2. Methods

For the present work, the glass $Cu_{65}Zr_{35}$ (at.%) was chosen because of extensive prior studies of this system [19,20]. MD simulations of the glass were based on an embedded-atom-method potential [21] that has been proven to reproduce satisfactorily the basic properties of Cu-Zr alloys, including metallic glasses. A system consisting of 31,250 atoms with periodic boundary conditions is initially melted at 2000 K and then cooled to 300 K at a rate of 2×10^{12} K s^{-1}. The simulations are performed at 300 K (with some at higher temperatures) with a time-step of 2 fs, in the isobaric-isothermal canonical ensemble with Nosé [22] and Andersen [23] daemons. Finally, equilibration for 2.2 ns in the microcanonical ensemble is used to ensure sufficient relaxation. For the tensile deformation we use a strain rate of 10^8 s^{-1} up to a strain of 10%, while in the lateral dimensions we impose strains corresponding to a Poisson ratio of 0.34 [24].

For the analysis of atomic coordination polyhedra, we use a procedure based on non-linear multi-dimensional minimization [25] of prototype clusters, taking each atom of the system as the potential center of a cluster. Based on previous studies [19,20] we consider cluster geometries that were found to have significant populations in the $Cu_{65}Zr_{35}$ metallic glass: icosahedral (ICO), rhombic dodecahedral (RD) and cuboctahedral (CUB). Because it is easier to obtain data not only on perfect but also on distorted and/or truncated clusters, this classification is more useful than that based on Voronoi polyhedra [26], which, however, we also used for comparison.

3. Results

The structural analysis reproduced the results reported in many previous studies (for example in Refs. [17,27]), that the atomic coordination is based on interconnected ICO-like clusters, most of which are distorted. Our present interest, however, is mainly in the detailed characterization of the time dependence of atomic positions. Fig. 2a shows the key finding, that for some atoms there is a clear alternation between two positions in each of which there is vibrational motion. The time dependence of atomic position seen in Fig. 2a is quite distinct from that found by Jakse et al. [16] (Fig. 3 in their paper) over very similar timescales and at the same temperature (300 K).

We determined the atomic positions from the locations of their Gaussian-like time distributions, thus avoiding the influence of thermal vibration. In contrast with a crystal, the metallic glass does not have a lattice with well-defined equilibrium positions. As a consequence, the rattling between two sites shows a wide distribution of distances (from 0.1 to more than 1.5 Å) and life-times (from 1.5 to more than 100 ps). This distribution is wider than the range of amplitude (0.3–0.6 Å) found by Jakse et al. [16] to contribute to the boson peak. As is emphasized in Fig. 2a, the motion is to-and-fro; consequently the net mass flow is practically negligible (i.e., as expected, no diffusion is found at 300 K). The rattling process revealed in Fig. 2a is shown with better time resolution in Fig. 2b. The alternation in atomic position is accompanied by changes in local coordination: the polyhedron around the rattling atom alternates between ICO and RD or CUB states as the atom moves to and fro.

It is remarkable that such rattling motions (with some amplitudes exceeding 1.5 Å) can occur, given that metallic glasses are so densely packed. There are no vacancies in metallic glasses, and their structure is considered to consist of efficiently packed clusters [21]. Our MD simulations do, however, reveal how such large-amplitude rattling is possible. Fig. 3 shows atomic sites (with vibration eliminated) in a local region. This shows that two or three neighboring atoms can perform concerted motions to accommodate large-amplitude rattling. In state 1 (Fig. 3a), atoms A and B, separated by 3.8 Å, are the central atoms in two touching (i.e. face-sharing) polyhedral clusters. In the rattling, atoms B, D, A and C have coordinated displacements of about 1 Å, comprising a string-like movement. Atom F is displayed in white because it was a neighbor of atom B in state 1, but it is not its neighbor in state 2, after atom B rattles to its other site. In the next stage (Fig. 3b), atom A does not move, while atom B returns to its initial location, and atom F becomes again part of its first-neighbor coordination shell. In this transition, five more atoms adjust their positions through small movements of the order of 0.3 Å. Finally (Fig. 3c), atom A returns near its initial location, followed by atom C. The movement is facilitated by atom D that moves downwards, followed by atom B. Again, a string-like movement can be identified. The atoms A and B are now first neighbors, at a distance of 2.7 Å, their two clusters are interpenetrating (i.e. the central atom of one is in the first-neighbor