Fundamental Link between $\beta$ Relaxation, Excess Wings, and Cage-Breaking in Metallic Glasses

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Abstract
In glassy materials, the Johari–Goldstein secondary (β) relaxation is crucial to many properties as it is directly related to local atomic motions. However, a long-standing puzzle remains elusive: why some glasses exhibit β relaxations as pronounced peaks while others present as unobvious excess wings? Using microsecond atomistic simulation of two model metallic glasses (MGs), we demonstrate that such a difference is associated with the number of string-like collective atomic jumps. Relative to that of excess wings, we find that MGs having pronounced β relaxations contain larger numbers of such jumps. Structurally, they are promoted by the higher tendency of cage-breaking events of their neighbors. Our results provide atomistic insights for different signatures of the β relaxation that could be helpful for understanding the low-temperature dynamics and properties of MGs.

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**ABSTRACT:** In glassy materials, the Johari-Goldstein secondary (β) relaxation is crucial to many properties, as it is directly related to local atomic motions. However, a long-standing puzzle remains elusive: why some glasses exhibit β relaxations as pronounced peaks while others as unobvious excess wings? Using microseconds atomistic simulation of two model metallic glasses (MGs), we demonstrate such a difference is associated with the amount of string-like collective atomic jumps. Relative to that of excess wings, we find that MGs having pronounced β relaxations contain larger numbers of such jumps. Structurally, they are promoted by the higher tendency of cages-breaking events of their neighbors. Our results provide atomistic insights for different signatures of the β relaxation that could be helpful for understanding the low-temperature dynamics and properties of MGs.

**TOC GRAPHICS**
If a liquid is cooled to temperatures below its melting point, it forms either a crystalline solid or a metastable supercooled liquid with sluggish dynamics. In the latter case, the structural (α) relaxation time increases enormously upon cooling and eventually reaches values typical for solid materials at the glass transition temperature. As the α relaxation time becomes so long that it appears as frozen in the glassy states, an additional process, called the Johari-Goldstein secondary (β) relaxation becomes the principal source of dynamics in the glassy state. It is related to local atomic motions in an otherwise rigid glass and hence of significance to the understanding of several crucial unresolved issues in glassy physics and material sciences (and see e.g. refs. for reviews). We note that there are some other processes also called secondary relaxation, but we follow the work of Ngai et al. to use the name “Johari-Goldstein β relaxation” to indicate they are sensitive to intermolecular interactions and not to intramolecular degrees of freedom.
One intriguing feature about β relaxation has attracted considerable attentions in the glass community. In some glass formers, the β relaxations manifest as distinct peaks as probed by mechanical or dielectric loss spectra; while in some other glasses, the β relaxations appear to be absent and, instead, excess contributions to the tails of α relaxations show up, which are the so-called excess wings\textsuperscript{15-19}. Notably, the behaviors of β relaxations are sensitive to chemical compositions and processing histories\textsuperscript{17-18, 20-28}. There a few empirical rules or correlations\textsuperscript{3, 17, 21-22} and especially the coupling model \textsuperscript{1, 3, 6} can rationalize the relationship between β relaxations and some other properties. Nevertheless, it is still not easy to predict which glasses would show pronounced β relaxations or excess wings from the first principle; it represents a challenging issue in glassy physics\textsuperscript{29-36}. Meanwhile, the presence of β relaxations (or excess wings) is related to a number of important properties of glassy materials, ranging from mechanical ductility of metallic and polymeric glasses\textsuperscript{1, 37-40} to stability of glassy medicines\textsuperscript{19, 41}. As a result, a mechanistic understanding of the distinctions between pronounced β relaxations and excess wings could have broad implications\textsuperscript{1, 10-11, 42-43}.

As indicated by experiments, β relaxations separate from the primary (α) processes upon cooling only after structural dynamics become slower than about a microsecond. Thus, in order to disentangle the β relaxation from α relaxation in simulations, the observation time must be of the order of microseconds or more\textsuperscript{2, 4}.

Recently, the structural mechanism governing the β relaxations have been investigated in a model MG by microseconds atomistic simulations\textsuperscript{29}, which show that string-like motions might be the origin of β relaxation in MGs. Also noted that string-like motions have been studies in several other models\textsuperscript{44-48}. In this connection, it could be revealing to study whether and how can
this mechanism rationalize the distinction between pronounced $\beta$ relaxation and excess wings in different MGs.

Figure 1 shows the storage- ($E'$) and loss moduli ($E''$) of the two systems determined from the MD simulations of dynamical mechanical spectroscopy (MD-DMS, see method). The first and second columns are the results for Ni$_{80}$P$_{20}$ and Y$_{65}$Cu$_{35}$ model MGs, respectively. Our main motivation for choosing these two models is that the atomic radii ratios for them are very similar, so the interatomic interaction strength could be responsible for the difference in dynamics.

As a typical example, Figure 1a shows the $E'$ (left axis) and $E''$ (right axis) as a function of temperature at a fixed oscillation period, $t_\omega = 100$ ns (related with frequency $f = 1/\ t_\omega$) for the Ni$_{80}$P$_{20}$ MG. Besides the dominant $\alpha$ relaxation (the rapid drop of $E'$ or the peak of $E''$ at $T \sim 550$ K), there is an additional peak in $E''$ at lower temperature, which can be assigned to the Johari-Goldstein $\beta$ relaxation. Figure 1b shows the similar data for the Y$_{65}$Cu$_{35}$ MG but it is difficult to identify a distinct $\beta$ relaxation peak, given that the $\alpha$ relaxation dominates the $E''$ curve. Only an excess contribution to the left flank of $\alpha$ relaxation might be discerned, that is, the excess wing. Figure 1c compares $E''$ for these two model MGs in a normalized plot where $E''$ and $T$ are scaled by the maximum value of $E''$ and its temperature. We find that the Ni$_{80}$P$_{20}$ MG has a pronounced $\beta$ relaxation, whereas only an excess wing appears for the Y$_{65}$Cu$_{35}$ case. The similar feature has been observed in other two different values of $t_\omega = 30$ (Figure 1d-f) and 10 ns (Figure 1g-i). The contrasting behaviors of the two model MGs provide an opportunity to elucidate their structural origins by MD simulations.
Figure 1. Probing $\beta$ relaxation and Excess wing in MGs. The storage ($E'$) and loss ($E''$) moduli of Ni$_{80}$P$_{20}$ model MG (a,d,g; i.e., the first column, data taken from ref.29), and Y$_{65}$Cu$_{35}$ mode MG (b,e,h; i.e., the second column) at different testing periodic $\omega$ as indicated. (c,f,i; i.e.; the third column) Compassions of normalized $E''$ as a function of scaled temperature at different values of $\omega$. The blue and yellow shaded areas are two functions to fit the global $E''$ of Ni$_{80}$P$_{20}$; however for Y$_{65}$Cu$_{35}$ the fittings are elusive and thus not conducted. The blue arrows in the middle column indicated temperature that $E''$ most likely deviate from a single peak profile. The red arrows in (a) and (b) indicated the glass transition temperature ($T_g$) independently determined from the volume-temperature relation during cooling.
Figure 2. Atomic displacements corresponding to $\beta$ relaxation and Excess wing in MGs.

Atomic configurations for (a) $T = 455$ K for Ni$_{80}$P$_{20}$ and (b) $T = 560$ K for Y$_{65}$Cu$_{35}$. Both the temperatures are at $0.85T_\alpha$ ($t_\omega = 100$ ns) for the two MGs. The color codes represent atomic displacements $u$ over 100 ns. (c) Statistics $p(u)$ of $u$ for the two model MGs. (d) Radial distribution function $g(r)$ of the model MGs; all the atoms are selected in determining $g(r)$. The inset of (c) is $p(u)$ against $u/r_p$, where $r_p$ is first peak position of $g(r)$.

Figure 2 (a) and (b) compare two atomic configurations at $T = 455$ K for Ni$_{80}$P$_{20}$ and $T = 560$ K for Y$_{65}$Cu$_{35}$, respectively. The temperatures are selected based on $0.85T_\alpha$ ($t_\omega = 100$ ns) (here, $T_\alpha$ is the peak temperature in Figure 1a-b) where the $\beta$ relaxation is most prominent for Ni$_{80}$P$_{20}$.
and where the excess wing onset appears for $Y_{65}\text{Cu}_{35}$ (see Fig.1c). The color codes represents the atomic displacement magnitude $u$ for every atom defined as $u_i(t) = |\vec{r}_i(t) - \vec{r}_i(0)|$ over a waiting time $t = 100$ ns. Heterogeneous dynamics are observed in both configurations, as can be directly seen in Figure 2a and b. Compared to $Y_{65}\text{Cu}_{35}$ (Figure 2b), the Ni$_{80}$P$_{20}$ MG (Figure 2a) contains more atoms with larger $u$. Figure 2c quantifies their difference by showing the probability density function $p(u)$ based on the statistics of $u$. Consistent with the images of Figure 2a and b, Ni$_{80}$P$_{20}$ has greater fraction of large $u$ than $Y_{65}\text{Cu}_{35}$. We also note that Ni$_{80}$P$_{20}$ has three discernable peaks separated by two valleys on $p(u)$, whereas there is only one peak and a hump for $Y_{65}\text{Cu}_{35}$. Figure 2d shows the pair distribution function $g(r)$ of the MGs, which relates to the probability of finding an atom at a distance $r$ away from a reference atom. Specific for Ni$_{80}$P$_{20}$, one can see that the positions of first and second peaks of $g(r)$ match exactly the second and third peaks of $p(u)$. This implies that atoms with large values of $u$ rearrange by cooperative jumps: one atom jumps to the position that is previously taken by another atom in its nearest or secondary neighbors. In other words, the jumps are from shell to shell. Similar signatures also hold for $Y_{65}\text{Cu}_{35}$ although less obvious (by about a factor of ten).

Figure 3a and b show the displacement vectors at the same temperature and waiting time as Figure 2. For clarity, the 2-dimension (2D) slices with thickness 1nm are displayed. We define displacement larger than $u_c = 1.8\text{Å}$ [corresponding to the first minimum in $p(u)$ in Figure 2c] as fast-moving atoms and they are indicated by red color, otherwise by blue for those slow-moving atoms. We find that many of the fast-moving atoms form string-like configurations. Figure 3c and d highlight the 3D string-like motions for the two MGs, other atoms that are not involved in the strings are removed for a clear view. One can see that Ni$_{80}$P$_{20}$ has more string-like configurations than $Y_{65}\text{Cu}_{35}$, and most of strings in the Ni$_{80}$P$_{20}$ MG are longer than that of
Y_{65}Cu_{35}. Such differences are supported by Figure 3e and f, which present the distribution of the number of atoms in a string $n_{str}$ for the two MGs. For example, the longest strings in Ni_{80}P_{20} contain about 10 atoms, while 4 atoms for that of Y_{65}Cu_{35}. Generally, the population decreases with $n_{str}$ and might be tentatively fitted by a function of exponential decay.

**Figure 3. String-like cooperative atomic jumps in MGs.** Atomic displacement vectors for (a) Ni_{80}P_{20} and (b) Y_{65}Cu_{35} MGs, the slice is 1 nm. String-like atomic displacements for (c) Ni_{80}P_{20} and (d) Y_{65}Cu_{35} MGs. Statistics of the number of atoms in string-like motions ($N_{str}$) for (e) Ni_{80}P_{20} and (f) Y_{65}Cu_{35} MGs. The red smooth curves in (e) and (f) are fitted by an exponential decay function.
Figure 4. Relationship between string-like motions and cage-breaking and $\beta$ relaxation.

The fraction of atoms in string-like configurations to the total number of fast-moving atoms ($N_{str}/N_{fast}$) as a function of time for different temperatures, (a) Ni$_{80}$P$_{20}$ (data taken from ref.29) and (b) Y$_{65}$Cu$_{35}$ MGs. The inset of (b) is the peak position $\tau_{str}$ as a function of temperature. The 2 dimensional contour plots of $N_{str}/N_{fast}$ are shown in (c) Ni$_{80}$P$_{20}$ and (d) Y$_{65}$Cu$_{35}$ respectively. (e) Schematic for the definition of cage-breaking. Cage-breaking fraction $C(T, t)$ for the two MGs (f) as a function of time $t$ for a fixed scaled temperature 0.85$T_\alpha$; (g) as a function scaled temperature for a fixed time $t = 100$ ns.

Figure 4 (a) and (b) shows the time evolutions of $N_{str} / N_{fast}$, the fraction of the number of atoms in string-like jumps to the number of fast-moving atoms as a function of time for different temperatures for the two model MGs. At each temperature, the values of $N_{str}/N_{fast}$ first increase...
with time but then decrease at longer times, exhibiting a finite maximum at a specific time, defined as $\tau_{str}$. Physically, $\tau_{str}$ measures the most probable time for the observation of the string-like motions in the background of fast-moving atoms. At the same time, the height of the peak [i.e., $N_{str} / N_{fast} (\tau_{str})$] grows with lowering temperatures, which indicate the increasing degree of cooperativity. Although both MGs follow the similar general trends, they have marked difference in the attainable values of $N_{str} / N_{fast} (\tau_{str})$. For instance, the Ni$_{80}$P$_{20}$ MG contains as much as twice string-like motions than the Y$_{65}$Cu$_{35}$ MG at the same scaled temperature.

Figure 4c recast the data of Figure 4a for Ni$_{80}$P$_{20}$ in term of a 2D contour plot where the values $N_{str} / N_{fast}$ are represented by color codes. The temperature and time of the $\beta$ relaxation as decomposed from Figure 1a, d and g are shown as discrete stars. We find that a remarkable match between the $\beta$ relaxation and the ridge of $N_{str} / N_{fast}$ as shown by the dashed line. This suggest that the $\beta$ relaxation occurs when most of the fast-moving atoms are string-like, implying the string-like motions could be the mechanism of $\beta$ relaxation in this Ni$_{80}$P$_{20}$ MG. Figure 4d report the similar findings in the Y$_{65}$Cu$_{35}$ MG. Because it has excess wings instead of pronounced peaks, the determination of $\beta$ relaxation is less accurate than that of Ni$_{80}$P$_{20}$, and we thus use the temperature as indicated by the arrows in Figure 1b, e and h, where the deviations from the tails of $\alpha$ relaxation are evident. We see that the excess wing is correlated with the ridge of $N_{str} / N_{fast}$ for this MG as well.

The above findings suggest that both the $\beta$ relaxation and the excess wing have same origin from the string-like cooperative jumps; their distinctions are from the different amounts of these jumps. They are also a reminiscent of “islands of mobility” scenario as previously suggested$^{2,50}$. However, we see this in a short time frame; it does not imply long time persistence of that pattern.
Why do the two model MGs have different amount of string-like motions that influence the behaviors of β relaxations? We consider the caging properties of as a precursor for them. In glassy states, most of the atoms are confined in transient cages formed by their neighbors. This prevents them from diffusing freely throughout the sample. Intuitively, to form string-like motions, the atoms must first escape from their cages. One can thus anticipate the caging properties could influence the string-like jumps and the β relaxations as a consequence\textsuperscript{42, 51-53}.

As schematically shown in Figure 4e, we define the number of atoms which break the cage as cage breaking fraction \( C(T, t = \delta t) \equiv N_{\text{lost}} / N_{\text{nb}} \) at a temperature \( T \) and over a time \( \delta t \), where \( N_{\text{nb}} \) is the number of atoms which are the nearest neighbors of one reference atom at \( t = 0 \); \( N_{\text{lost}} \) the number of atoms that no longer the nearest neighbors at \( t = \delta t \) but they were previously the nearest neighbors at \( t = 0 \). We use the Voronoi tessellation method to identify the nearest neighbors.

Figure 4f shows the \( C(T, t) \) as a function of waiting time \( t \) at the same scaled temperature \( T = 0.85 T_\alpha (t_\omega = 100 \text{ns}) \) for the Ni\textsubscript{80}P\textsubscript{20} \((T = 455 \text{ K})\) and Y\textsubscript{65}Cu\textsubscript{35} \((T = 560 \text{ K})\), respectively. We find that at short time \( t < 1 \text{ ns} \), the values of \( C(t) \) are low for both MGs. However, considerable difference between them develops for longer \( t \), and notably, \( C(t) \) the Ni\textsubscript{80}P\textsubscript{20} MG increases more rapidly than that of Y\textsubscript{65}Cu\textsubscript{35}. Particularly, for \( t = 100 \text{ ns} \) (which is the timescale of the β relaxation as well as most probable time of string-like motions at the considered temperature), \( C(t) \) is more than 0.15 for Ni\textsubscript{80}P\textsubscript{20} while \( C(t) = 0.09 \) for the Y\textsubscript{65}Cu\textsubscript{35} MG, indicating the cages of the Ni\textsubscript{80}P\textsubscript{20} MG are more prone to break. Additional information can be gained from Figure 4g which reports \( C(T, t=\delta t) \) as a function of temperature scaled by \( T_\alpha (t_\omega = 100 \text{ ns}) \) for a fixed \( \delta t = 100 \text{ ns} \) for the two MGs, their difference is evident in the temperature range relevant for the β relaxations.
Recently, the connections between $\beta$ relaxations and the caging properties in different glasses\textsuperscript{42, 51-53} have been discussed based on the coupling model. Our findings provide a direct atomistic picture. We may attribute the excess wing to be less developed $\beta$ relaxations as the atoms start to break the cage quite late and cannot develop the string-like motions since structural $\alpha$-relaxation arises soon, bringing to cage collapse and global diffusions.

In summary, by atomistic simulations of two model metallic glasses up to the timescale of microseconds, we offer a structural basis for the difference between the pronounced $\beta$ relaxations and excess wings in metallic glasses. The emerging physical picture is that string-like cooperative atomic jumps are directly correlated to both the $\beta$ relaxation and the excess wing, and thus they have the same origin regarding the cage-breaking process which might depend on the interatomic potentials\textsuperscript{21, 54}. Their distinctive behavior stems from the richness of these string-like motions, which is linked to the cage-breaking tendency as a precursor. Future studies should address how local properties impact cage-breaking and whether this concept applies to other classes of glass formers. Some previous simulations indicated that string-like motions might be abundant in some atomic\textsuperscript{44, 47} and polymeric models\textsuperscript{48} but scarce in a covalent model\textsuperscript{55}, it would be interesting to see whether they are correlated to the Johari-Goldstein $\beta$ relaxation as well.

**Simulation Method**

We use the LAMMPS software to conduct MD simulations. Our model system contains $N = 32000$ atoms. Two model systems, namely Ni\textsubscript{80}P\textsubscript{20} and Y\textsubscript{65}Cu\textsubscript{35} are studied. They interacted with an embedded atom method potential from Sheng et al\textsuperscript{56-57} and Wang et al\textsuperscript{58} respectively. Some of the data (i.e., Fig.1a, d, g and Fig. 2a) of the Ni\textsubscript{80}P\textsubscript{20} have been published\textsuperscript{29} but they are included (and re-plotted) for the purpose of a contrast between the two models. The samples
were prepared by quenching a liquid from 1000 to 200 K at a rate of 0.1 K/ns. We used \( NPT \) ensembles during the quenching. The external pressure is adjusted to around zero. Periodic boundary conditions were applied for all the simulations.

Dynamics of \( \beta \) relaxations are studied by an approach of MD simulations of dynamical mechanical spectroscopy (MD-DMS)\(^{59-60}\) that numerically reproduces the protocol of real DMS experiments\(^{11-12}\). Specifically, at a temperature \( T \), we apply a sinusoidal strain \( \varepsilon(t) = \varepsilon_A \sin(2\pi t / t_\omega) \) with a period \( t_\omega \) (related to frequency \( f = 1 / t_\omega \)) and a strain amplitude \( \varepsilon_A \), along the \( x \) direction of the model MG and the resulting stress \( \sigma(t) \) and the phase difference between stress and strain \( \delta \) are measured and fitted with \( \sigma(t) = \sigma_0 + \sigma_A \sin(2\pi t / t_\omega + \delta) \). From these values, storage \((E')\) and loss \((E'')\) moduli are calculated according to \( E' = \sigma_A \sin \delta / \varepsilon_A \) and \( E'' = \sigma_A \cos \delta / \varepsilon_A \), respectively. We use strain amplitude \( \varepsilon_A = 0.71\% \) for all the MD-DMS, which ensures the deformation is in the linear response regime and \( E', E'' \) are independent of \( \varepsilon_A \) within resolution.

Notes

The authors declare no competing financial interests.

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