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Heterogeneous dynamics of metallic glasses

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ABSTRACT

Heterogeneous dynamics in the flow of supercooled metallic liquids are revealed as the oscillated mechanical response in compression and evidenced to be consistent with the range of medium length scales over which structural rearrangements occur detected by small angle X-ray scattering (SAXS) in heating from room temperature to the supercooled liquid region. This range of medium length scales is suggested to be the structural origin of the heterogeneous dynamics of metallic glasses.

A non-equilibrium transition from fluidity to rigidity [1], i.e., jamming, prevails in a wide variety of disordered systems [2], including granular media [3], colloidal suspensions [4], molecular systems [5]. While the disordered liquid-like structure remains basically unchanged at the transition, further exploration of the phase space is precluded by the glasslike arrest of their dynamics [1,6–8]. Approaching the jamming limit, the development of heterogeneous atomic dynamics in glasses [2,4,9] is indicated by the structure heterogeneity, i.e., coexistence of liquid-like and solid-like regions [10] of medium length scale (1–3 nm) [11,12]. *In situ* scattering investigations [13–15] have already revealed the critical role played by atomic rearrangements underlying the structure heterogeneity in the flow (i.e., unjamming) of metallic glasses [1]. However, the inherent liquid-like or solid-like local configurations do not correlate well with the heterogeneous atomic rearrangements [16,17], implying that a static view of the structure heterogeneity is not enough to recognize the arrest of dynamics in the fluidity-to-rigidity transition. Rather, unjamming (e.g., flow or glass-to-liquid transition of glasses) and the underlying dynamics would be crucial. In this work, the flow and structure of supercooled metallic liquids are respectively examined via uniaxial compression and *in situ* small angle X-ray scattering (SAXS) in heating. The range of medium length scales over which structural rearrangements occur observed in SAXS is suggested to be the structural origin of the heterogeneous dynamics of metallic glasses.

Rods of 3 mm in diameter of bulk metallic glasses $Zr_{58.5}Cu_{15.6}Al_{10.3}Ni_{12.8}Nb_{2.8}$ (Vit106a), $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit1), $Zr_{55}Cu_{30}Al_{10}Ni_5$ (Zr55) and $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ (ZrBe) were prepared by copper mould casting. Cylindrical specimens of aspect ratio 1:1 [18] were carefully prepared to ensure the two ends being parallel. The high temperature compressive stress–strain (SS) curves were obtained above each BMG's $T_{g\text{-}end}$ (the end of glass transition temperature) with a Zwick/Roell mechanical testing system. *In situ* SAXS tests with increasing temperature on Vit106a and Vit1 were conducted at beamline BL16B1 of Shanghai Synchrotron Radiation Facility with a photon energy of 10 keV (wavelength 1.24 Å) to monitor the amorphous structure evolution.

The SS curves of $Zr_{58.5}Cu_{15.6}Al_{10.3}Ni_{12.8}Nb_{2.8}$ (Vit106a), $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit1), $Zr_{55}Cu_{30}Al_{10}Ni_5$ (Zr55) and $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ (ZrBe) BMGs are shown in Fig. 1(a)–(d), respectively. All these BMGs show similar stress–strain (SS) $\sigma-\varepsilon$ responses with increasing strain rates. For example, Fig. 1(a) shows the SS curves for Vit106a. With increasing strain rate, the SS curves change from the stress σ increasing monotonously to a plateau at strain rate $\dot{\varepsilon}$ of an order of 10^{-3} s^{-1}, to stress overshoot of an order of 10^{-2} s^{-1}, and finally to stress overshoot followed by undershoot, i.e. oscillation, of an order of 10^{-1} s^{-1}. These oscillations have been observed at strain rate sensitivity $m=\partial \lg\sigma/\partial \lg\dot{\varepsilon}\leqslant 0$ near T_g and reported to originate [19] from the flow dynamics of structure heterogeneities of a size of 1–3 nm (Figs. S1 and S2 in Supplementary) which act as flow defects [20]. Vit106a and Vit1 show localized shear fracture rather than homogeneous flow (i.e., jammed [1,7]) at strain rates above 0.5 s^{-1} and 0.7 s^{-1}, respectively. Although there is a resemblance born in Fig. 1(a) and (b), it is noticed that, by comparing the SS curves of Vit106a to Vit1,

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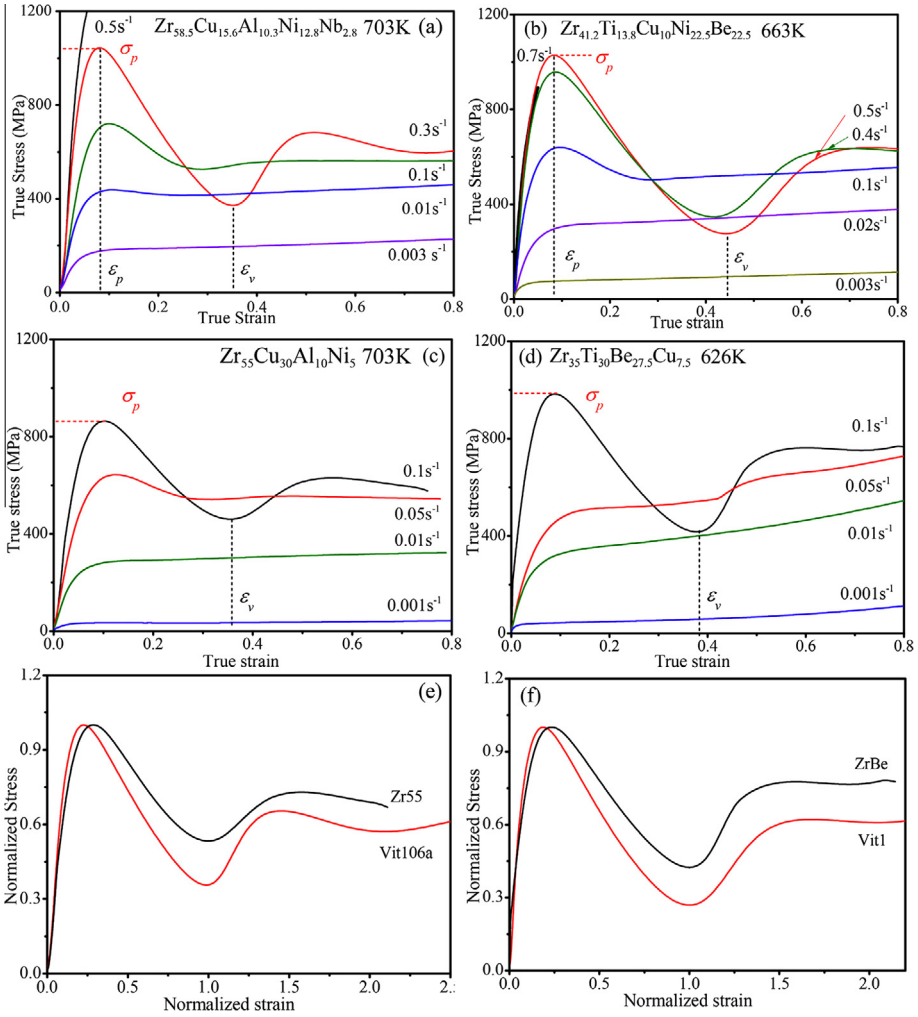

Fig. 1. SS curves for (a) Vit106a, (b) Vit1, (c) Zr55, and (d) ZrBe BMGs; normalized SS curves (e) for Vit106a and Zr55, (f) for Vit1 and ZrBe, where the stress is normalized by the peak stress σ_p on the first stress overshoot, the strain is normalized by the width of the first stress overshoot ε_v.

stronger oscillations with a smaller period in the SS curves of Vit106a emerge than in the SS curves of Vit1, suggesting different flow dynamics of these glasses. This is also supported by the conclusion that the widths of the first stress overshoot ε_v (0.35 and 0.44 for Vit106a and Vit1, respectively) depend on the size of the structure heterogeneity [21,22]. To confirm the observed SS response in flow, SS curves of Zr55 and ZrBe are also shown in Fig. 1(c) and (d). Interestingly, Zr55 and ZrBe behave similar to Vit106a and Vit1, respectively. For comparison, the SS curves with oscillations are collected into Fig. 1(e) and (f) with the stress σ normalized to σ_p and the strain ε normalized to ε_v to remove the effect of strain rate $\dot{\varepsilon}$, since $\dot{\varepsilon}$ affects merely ε_v and σ_p, not the shape of oscillation near jamming (See Fig. 1(b) 0.4 s^{-1} and 0.5 s^{-1}). It shows that Vit106a and Zr55 exhibit different flow dynamics from Vit1 and ZrBe.

For an overview on the flow properties of Vit106a and Vit1, Fig. 2(a) and (b) shows the fitted master curves of which the constitutive equation is as follows [23]: $\eta/\eta_N = 1 - \exp\left(-(\alpha/(\dot{\varepsilon}\cdot\eta_N))^{\beta}\right)$, where $\eta = \sigma_s/3\dot{\varepsilon}$ is the apparent viscosity; σ_s is steady flow stress; η_N is the Newtonian viscosity; α and β are fitting parameters. It can be seen that Vit106a and Vit1 supercooled metallic liquids exhibit well fitted flow properties similar to that of polymers etc. and extremely alike features with the fitting parameters being almost the same. Recalling the oscillated responses of supercooled metallic liquids, it is concluded that the oscillation rarely effects on the final steady flow state for no feature appears in the oscillated regime indicated by the ellipses and reveals the dynamics beneath unjamming.

Fig. 3(a) shows the SAXS patterns of the as-cast Vit106a and Vit1 at room temperature, where the rise of the intensity $I(q)$ at small scattering vector q is connected to the structure heterogeneity on medium length scale [24]. Similar patterns have also been observed in other metallic glasses [25,26]. Like in Fig. 2 which shows similar flow properties, the inset of Fig. 3(a) shows a similar gyration radius of Vit1 (R = 1.28–2.58 nm) and Vit106a (R = 1.00–2.31 nm) evaluated by the fitting of $\ln(I) - q^2$ curve with Guinier's Law [27] ($I(q) = I_0 \exp(-q^2R^2/3)$, I_0 is a coefficient) (Figs. S3 and S4 in Supplementary). Fig. 3(b) and (c) shows the SAXS patterns of Vit106a and Vit1 at different temperatures from 298 K to above T_g, respectively. As reported that structure heterogeneity does not correlate well with the spatially distributed dynamics [16,17], the $\ln(I) - q^2$ curves of Vit106a and Vit1 are hardly distinguishable with increasing temperature indicating an almost constant R (Fig. S5 in Supplementary). However, as indicated by the arrows, it is interesting to note that the range $\Delta q = q_A - q_B$ where $I(q)$ increases of Vit106a and Vit1 exhibit a prominent difference, in contrast. In the insets of Fig. 3(b) and (c), Δq is determined to be 0.121 nm^{-1} for Vit106a and 0.162 nm^{-1} for Vit1 (Figs. S6 and S7 in Supplementary), respectively. In accord with Fig. 1, as q is a measure of length scales

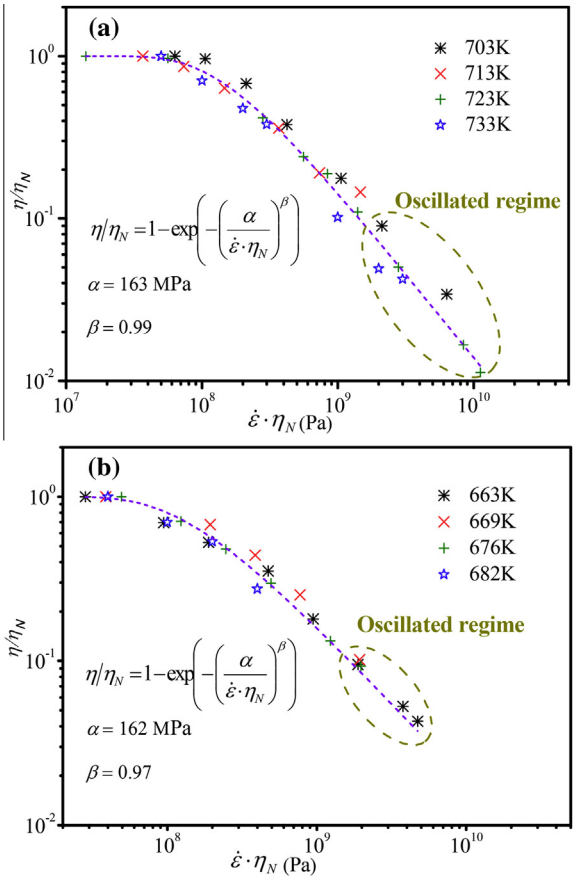

Fig. 2. Master curves for flow properties of (a) Vit106a and (b) Vit1. The ellipses indicate the oscillated SS response regime.

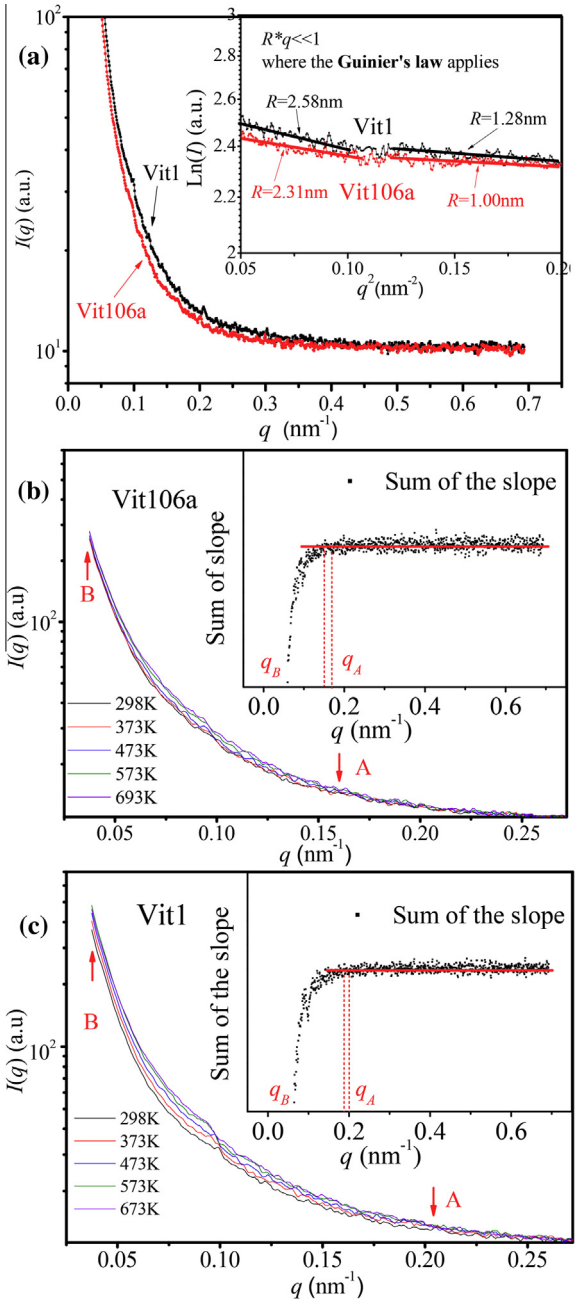

Fig. 3. SAXS patterns for Vit106a and Vit1 BMG (a) at room temperature, the inset shows the fitting via Guinier's Law; (b) Vit106a BMG at various temperatures into supercooled liquid region; (c) Vit1 BMG at various temperatures into supercooled liquid region. The insets in (b) and (c) show the determination of the range $\Delta q = q_A - q_B$ for Vit106a and Vit1 BMG (See Supplementary) over which structural rearrangements occur during glass transition.

of the jammed structure in scattering theory, a smaller Δq of Vit106a indicates its narrower range of length scales of structural rearrangements and again implies its different dynamics from Vit1 in heating.

To confirm the results observed above, since the heterogeneous dynamics in unjamming via either stress or temperature are of the same structure origin [11] and for the stress–temperature scaling in glass transition: $T/T_0(\eta) + [\sigma/\sigma_0(\eta)]^2 = 1$ (T is temperature, $T_0(\eta)$ is the temperature where viscosity is equal to η when $\sigma = 0$, and $\sigma_0(\eta)$ is the shear flow stress where viscosity is equal to η when $T = 0$ [28]), where equivalent effects of stress and temperature on the structure of glasses in unjamming are suggested, we have checked the consistency of the results in Fig. 1 and Fig. 3.

Taking Δq as an indication of the heterogeneous dynamics in heating, a counterpart in flow is required for comparison. Approaching yielding [13], it has been reported that the length scale dependent atomic strain ε_{atomic} of the jammed structure as illustrated in Fig. 4 (r dependent ε_{atomic}, Fig. S1 in Supplementary, where r is the distance of different atom shells from average atom on radial distribution function (RDF), ε_{atomic} is calculated by the shift of the peaks of RDF under load from scattering measurements [13]) arising from the structural rearrangements over medium length scales of 0.4–2 nm shows increasing r dependence and heterogeneity with increasing stress [13,14] and plays crucial role in the SS response. A characteristic range r_{range} over which the atomic strain ε_{atomic} increases from 0 to the macroscopic strain will develop from short length scale into medium length scale [13]. It has also been reported [29] that upon yielding, structural rearrangements [30] on this range of medium length scales will *connect the local atomic rearrangements and the macroscopic strain* and promote the macroscopic flow, i.e. bridging atomic dynamics to continuum mechanics [12]. As also suggested in Ref. [21], in the flow of supercooled metallic liquids, taking the left-flank of stress overshoot ε_p as the elastic strain required to overcome the energy barrier [30–32], the right-flank $\Delta\varepsilon = \varepsilon_v - \varepsilon_p$ (in Fig. 1(a) and (b)) should reflect the structural rearrangements over r_{range} underlying flow as shown in Fig. 4. The r_{range} should be proportional to $\Delta\varepsilon$ and be the length scales of the structural α-relaxation [12] where β relaxation events percolate. Therefore, the heterogeneous dynamics in heating and in flow can be compared utilizing the ratio of the width of stress overshoot $\varepsilon_{v-\text{Vit1}}/\varepsilon_{v-\text{Vit106a}} \approx 0.795$ and the ratio

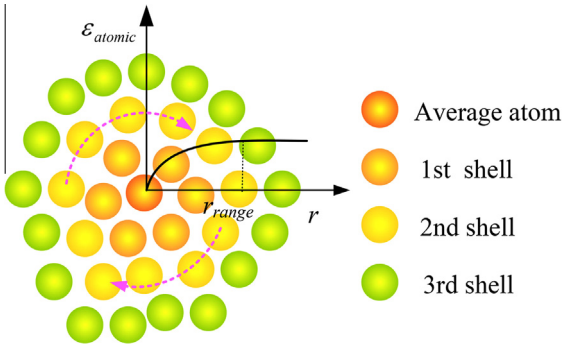

Fig. 4. A schematic illustration of the correlation between the range of length scale dependent atomic strain and the right-flank of stress overshoot $\Delta\varepsilon = \varepsilon_v - \varepsilon_p$ (in Fig. 1(a) and (b)). r from radial distribution function (RDF) of amorphous solids is the distance from average atom, ε_{atomic} is the length scale dependent strain calculated by the shift of the peaks of RDF under load. Upon yielding, when the energy barrier for structural rearrangements is overcome as the stress reaches the peak of the stress overshoot σ_p, unjamming and structural rearrangements occur overwhelmingly over the length scale indicated by r_{range} which should be proportional to $\Delta\varepsilon$.

of the range of medium length scales where structural rearrangements occur $\Delta q_{\mathrm{Vit106a}}/\Delta q_{\mathrm{Vit1}} \approx 0.746$ for Vit1 and Vit106a. It can be seen that the two ratios are reasonably close. Furthermore, with the postulation that the right flank of the stress overshoot $\Delta\varepsilon = \varepsilon_v - \varepsilon_p$ indicates the range of length scales where structural rearrangements occur, the ratio $\Delta\varepsilon_{\mathrm{Vit106a}}/\Delta\varepsilon_{\mathrm{Vit1}} = 0.75$ matches better the ratio $\Delta q_{\mathrm{Vit106a}}/\Delta q_{\mathrm{Vit1}} \approx 0.746$ for Vit1 and Vit106a.

Therefore, it is concluded that Vit106a exhibits different heterogeneous dynamics from Vit1 and that corresponding to Δq, $\Delta\varepsilon = \varepsilon_v - \varepsilon_p$ represents the range of medium length scales over which structural rearrangements occur and indicates the heterogeneous dynamics in the flow of supercooled metallic liquids. Larger Δq or $\Delta\varepsilon$ would probably represent a more homogenous dynamics, for the atomic rearrangements occur on a broader length scale range. The characteristic range of medium length scales of structural rearrangements rather than the static jammed structure is essential to understand the arrest of dynamics in jamming. As the dynamic heterogeneity induced by flow or cooling exceeds the intrinsic dynamic heterogeneity of the supercooled liquids indicated by the results of SAXS in Fig. 3(b) and (c) with increasing flow rate [13] or decreasing temperature, the atomic kinetics will be arrested to exhibit singularity in flow (Brittle fracture in Fig. 1(a) and (b)), i.e., jammed [1,7]. It is also crucial to note that the stress overshoots indicating the intrinsic heterogeneous dynamics of supercooled metallic liquids are only those observed on the SS response near jamming. Finally, this work suggests a way to reveal the heterogeneous dynamics of metallic glasses and supports the correlation between flow and structural relaxation of metallic glasses from the aspect of spatial scales [12] of the two processes [33].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.scriptamat.2015.05.034.

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