Unified Criterion for Temperature-Induced and Strain-Driven Glass Transitions in Metallic Glass

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In a model metallic glass, we study the relaxation dynamics in both the linear and the nonlinear response regimes by numerical simulations of dynamical mechanical spectroscopy and analyze the atomic displacement statistics. We find that the primary (α) relaxation always takes place when the most probable atomic displacement reaches a critical fraction (~20%) of the average interatomic distance, irrespective of whether the relaxation is induced by temperature (linear response) or by mechanical strain (nonlinear response). Such a unified scenario, analogous to the well-known Lindemann criterion for crystal melting, provides insight into the structural origin of the strain-induced glass-liquid transition.

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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, further cooling will eventually result in the formation of a noncrystalline solid, a glass [1–5]. While the liquid-to-crystal transition is a first-order phase transition, the supercooled liquid-to-glass transition is a kinetic event based on relaxation times growing rapidly as the temperature is decreased. The underlying relaxation dynamics of the liquid-glass transition is known as primary (α) relaxation and constitutes a central topic and long-standing issue in glassy physics [1–6].

Recently, nonlinear relaxation dynamics have become a topic of interest and are being actively discussed in glassy physics [7–12]. It has been recognized that mechanical strain (or stress) within the nonlinear response regime plays a similar role as temperature in the dynamics of α relaxation in many kinds of glass-forming materials, including colloidal glasses [13,14], granular systems [7], polymers [15], metallic glasses (MGs) [16,17], and numerical models [18]. Large mechanical strain can accelerate relaxation dynamics and even induce glass-liquid transition athermally, and thereby appears to play a role analogous to that of temperature within the linear response regime. More recently, we have shown that temperature and strain might have subtle differences in altering relaxation dynamics in a CuZr model MG[8]. Specifically, a large strain amplitude makes a fragile liquid become stronger, reduces dynamical heterogeneity at the glass transition, and broadens the loss spectra asymmetrically, in addition to speeding up the relaxation dynamics.

Despite these findings, it is still not clear what the structural origin for the intriguing phenomenon of strain-induced glass-liquid transition is, or if there is a unified structural scenario for the temperature and stress- or strain-induced (more general, linear and nonlinear) α relaxations [19].

A useful theory that might be relevant for this issue is the Lindemann criterion for melting of crystalline solids [20,21]. It considers the vibration of atoms in the crystal as a precursor to melting: When a temperature rise causes the amplitude of vibrational displacement of atoms to reach a critical value relative to the average interatomic distance, melting occurs. For most materials, this threshold value lies in the range of 10%–20%, depending on factors such as the nature of interaction and the magnitude of quantum effects. Some previous experimental and numerical studies indicate that the Lindemann criterion might be applicable to the issue of the liquid-glass transition (in the linear response regime) [22–26] though with some controversies [27–31].

In this work, using numerical simulations of dynamical mechanical spectroscopy together with structural analysis, we show that a Lindemann-like criterion holds universally for the α relaxation, and remarkably, irrespective of whether the relaxation is induced by temperature in the linear response regime or driven by mechanical strain in the nonlinear response regime. We find the α transition always occurs when the most probable atomic displacement reaches about 20% of the average interatomic distance. Such a unified scenario provides a simple yet clear structural origin of the strain-induced glass-liquid transition.

We use molecular dynamics (MD) simulations to study the relaxation dynamics of a model $Ni_{80}P_{20}$ MG which contains 32 000 atoms that interact with an embedded atom method potential as developed by Sheng *et al.* [32,33]. The glassy sample was prepared by quenching a liquid from 1500 K at a rate of 10^{10} K/s. The resulting glass transition temperature T_g is about 530 K at this cooling rate, inferred from the volume changes against temperature T as shown in the inset of Fig. 1. Because of the high cooling rate, this

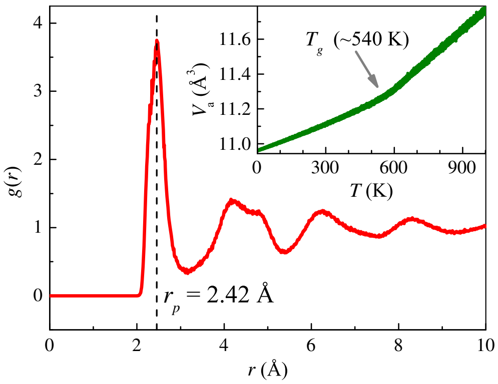

FIG. 1 (color online). Radial distribution function $g(r)$ of $Ni_{80}P_{20}$ MG at $T = 300$ K. Inset: atomic volume V_a as a function of temperature during the quenching process.

T_g is higher than values derived from calorimetry using rates of about 20 K/min. Figure 1 shows the pair distribution function $g(r)$ of the MG at $T = 300$ K, which relates to the probability of finding an atom at a distance r away from a reference atom. The position of the first peak of $g(r)$ indicates that the average nearest interatomic distance is $r_p = 2.42$ Å.

Relaxation dynamics of the MG are studied by approaches of MD simulations of dynamical mechanical spectroscopy (MD-DMS) [34] that numerically reproduces the protocol of real DMS experiments [35,36]. Specifically, at a temperature T, we apply a sinusoidal strain $\epsilon(t) = \epsilon_A \sin(2\pi t/t_\omega)$, with a period t_ω (related to frequency $f = 1/t_\omega$) and a strain amplitude ϵ_A, along the x direction of the model MG, and the resulting stress $\sigma(t)$ and the phase difference δ between stress and strain are measured. From these values, both the storage (E') and loss (E'') modulus are calculated. To study the strain effects on glassy dynamics, we intentionally vary ϵ_A from about 0.6% to 11%, covering both the linear and the nonlinear response regimes, which roughly correspond to the elastic and viscoelastic-plastic deformation regimes, respectively. For all the MD-DMS simulations, we computed the atomic displacement $u(\delta t) = \|\vec{r}(\delta t) - \vec{r}(0)\|$ for each atom during the time interval of $\delta t = t_\omega$. This choice of δt is meant to avoid atomic displacements due to the overall deformations applied by the MD-DMS. We note that the definition of u includes both the vibrational and the diffusive atomic movements. The probability density function $p(u) = [P(u + \delta u) - P(u)]/\delta u$ is calculated on the basis of these u values, where $P(u)$ is the distribution that quantifies the probability of finding $X \le u$. We used $\delta u = 0.01$ Å for all the calculations and 10 cycles for each MD-DMS measurement.

Figure 2(a) shows an example set of E'' curves as a function of T for a selected combination of $\epsilon_A = 1.25\%$ (which is in the linear response and elastic deformation regimes) and t_ω ranges from 100 to 10 000 ps (or $f = 0.1$ to 10 GHz). All these curves exhibit typical features of α relaxations and are consistent with experimental DMS results [35,36], i.e., the asymmetrical peak of E'' that signals the transition from a glassy state to a supercooled liquid state. Figure 2(b) shows the typical probability

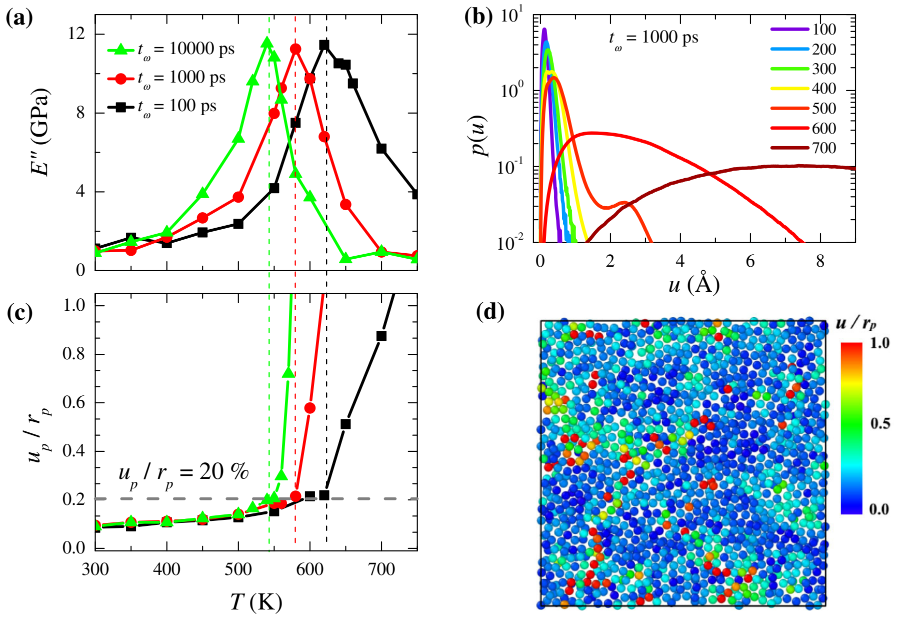

FIG. 2 (color online). MD-DMS and structural analysis in linear response regime. (a) Loss (E'') modulus as a function of temperature (T) at a strain amplitude $\epsilon_A = 1.25\%$. (b) Typical curves of the probability density function $p(u)$ for atomic displacement u at temperatures as indicated. (c) The peak position u_p as a function of temperature. (d) A 2D slice of the atomic configuration at $T = 500$ K, $t_\omega = 1000$ ps, with color code on each atom representing the value of u/r_p, and the box size is about 7 nm in each dimension.

density function $p(u)$ of atomic displacement u during MD-DMS for different T (where $\epsilon_A = 1.25\%$ and $t_\omega = 1000$ ps). One can see that $p(u)$ has a sharp peak at low T but it gets widened when $T > 600$ K. Both the peak position u_p and the peak intensity depend on T. Obviously, u_p represents the most probable atomic displacement for all the atoms.

Figure 2(c) quantitatively summarizes how the most probable atomic displacement scaled by average nearest interatomic distance u_p/r_p varies with T for the same t_ω as Fig. 2(a). We find u_p/r_p increases drastically when T approaches T_α. This implies a transition from vibrational dominant to diffusive dominant atomic motions. Similar features were observed in the melting of crystalline solids [37,38]. Remarkably, the temperature where u_p/r_p has a discontinuity occurs at $T = T_\alpha$ as indicated by vertical dashed lines through Figs. 2(a) and 2(c). At the same temperature, we find u_p/r_p reaches 0.20 ± 0.01. Such a value agrees with the Lindemann criterion for melting of crystalline materials as mentioned above. In other words, the above analysis demonstrates that α relaxation takes place when the most probable atomic displacement reaches about 20% of the average interatomic distance in the model $Ni_{80}P_{20}$ MG. This result connects the Lindemann-like criterion with the α relaxation in the linear response regime. We note the subpeak for $T = 500$ K in Fig. 2(b) is a signature of dynamically heterogeneity as confirmed by Fig. 2(d), which shows the atomic displacement u is inhomogeneously distributed.

Next, we study the relaxation dynamics in the nonlinear response regime and assess whether the above scenario still holds. The nonlinear dynamics are induced and probed simultaneously by the MD-DMS with controlled ϵ_A. Figure 3(a) shows the typical curves of E'' and u_p/r_p as a function of ϵ_A for $T = 400$ K and $t_\omega = 1000$ ps. One can see that for $\epsilon_A \leq 1\%$, both E'' and u_p/r_p are independent of ϵ_A, indicating the model MG responds linearly to the external periodic deformations [39]. However, with further increase of ϵ_A, nonlinear response sets in, E'' first increases and then decreases, with a peak around $\epsilon_A = 3.7\%$, and u_p/r_p increases rapidly after that. These features, phenomenologically similar to Figs. 2(a) and 2(c), indicate that the model MG enters into a liquidlike state driven by mechanical strain; i.e., the α relaxation takes place at $T = 400$ K under $\epsilon_A = 3.7\%$, which is 180 K lower than for the case of $\epsilon_A = 1.25\%$, as shown in Fig. 2(a), and is 140 K lower than T_g as shown in the inset of Fig. 1. Experimentally, similar behaviors in terms of loss shear modulus have been observed in colloid glasses [40–43]. Overall, the similarity of the curves between Fig. 3(a) and Figs. 2(a) and 2(c) suggests that strain could take the similar role as temperature in effecting the relaxation dynamics and the corresponding atomic movements. It also implies a connection between strain-driven and temperature-induced liquid-glass transition from the perspective of structural rearrangements.

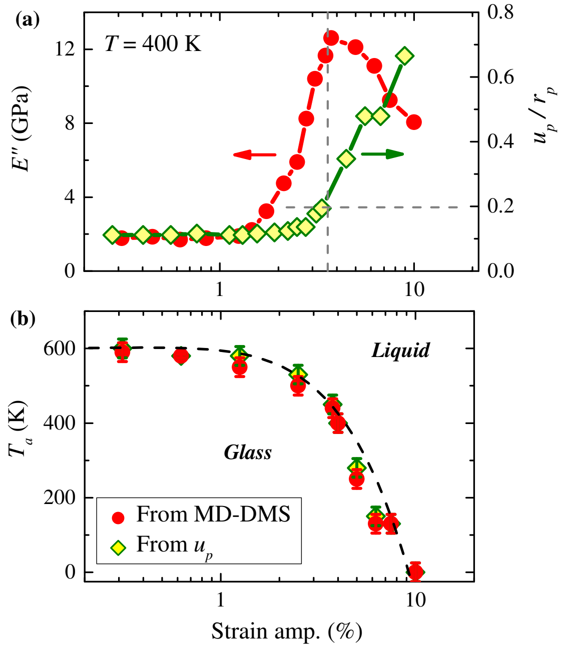

FIG. 3 (color online). MD-DMS and structural analysis in nonlinear response regime. (a) Loss (E'') modulus and u_p/r_p as a function of strain amplitude at a period $t_\omega = 1000$ ps and $T = 400$ K. The vertical and horizontal dashed lines indicates the peak position of E'', and the Lindemann criterion with $u_p/r_p = 20\%$, respectively. (b) Strain amplitude effects on the temperature of α relaxation T_α at $\tau_\alpha = t_\omega = 1000$ ps. The dashed line is drawn as a guide to the eyes.

Especially, we find that the peak of E'' and the Lindemann criterion $u_p/r_p = 20\%$ occur at the same strain amplitude, as marked through Fig. 3(a). This demonstrates that the Lindemann-like criterion for α relaxation, as found in the linear response regime, is also applicable to the nonlinear response regime even though the relaxation dynamics are caused by mechanical strain instead of temperature.

We have also conducted a series of additional simulations for other combinations of T and ϵ_A at $t_\omega = 1000$ ps. The results can be summarized as the ϵ_A dependency of T_α determined from the peak temperature of E'' and the temperature where $u_p/r_p = 20\%$ (i.e., the Lindemann criterion), respectively. As shown in Fig. 3(b), we find these two data sets overlap with each other and follow the same trend. This shows that T_α is independent of ϵ_A within the linear response regime ($\epsilon_A < 1\%$), whereas for larger ϵ_A located within the nonlinear response regime, T_α decreases pronouncedly and is practically zero when ϵ_A approaches 10%. These results provide evidence that strain can accelerate the relaxation dynamics and support the notion of a mechanically driven liquid-glass transition. Meanwhile, this result demonstrates again that both in the linear and nonlinear regimes α relaxations universally take place when the most probable atomic displacement reaches ~20% of the average interatomic distance.

Why does the Lindemann criterion apply to both the linear and the nonlinear relaxation dynamics of glasses, although it was originally proposed for melting transitions of crystals? We note that the Lindemann criterion in fact corresponds to the instability of a solid—irrespective if it is crystalline or glassy in nature, and is not limited to the equilibrium transition [37,44–46]. For crystalline solids, the instability of the crystalline lattice and melting take place at the same time which is a phase transition, while for glassy materials the instability of the disordered structure corresponds to α relaxation which is a dynamical event. Moreover, this instability should be independent of the nature of the driving force, which can be either heat-driven or mechanical work. This notion is validated by Fig. 3(b), which shows that the 20% criterion for structural relaxation holds even at temperatures near zero, i.e., for transitions that are almost entirely athermal.

Structurally, both glassy and crystalline solids feature local caging of their neighbor constituent particles and the liberation of caging might be a plausible origin of the unified Lindemann criterion for the linear and nonlinear liquid-glass transition as well as the melting of crystals [31,47]. Such arguments also suggest the Lindemann criterion must have wider implications than its original application as a melting criterion.

Finally, we note that our findings are not limited to the $Ni_{80}P_{20}$ model MG; we have conducted a similar analysis for a $Cu_{65}Zr_{35}$ model MG in the linear and nonlinear relaxation regime (the original data from Refs. [34] and [8], respectively.) and found that the temperature- and strain-induced liquid-glass transitions universally take place when $u_p/r_p \sim 22\%$ for the $Cu_{65}Zr_{35}$ MG. The slight difference in the Lindemann ratio might come from their different interaction potentials [48]. Nevertheless, the universal Lindemann feature for temperature- and strain-induced liquid-glass transition are essentially the same for the two model MGs.

In summary, by MD-DMS with varied strain amplitude and structural analysis for model MGs, we reveal that the α relaxation universally takes place when the most probable atomic displacement reaches a critical fraction (~20%) of the average interatomic distance, irrespective of whether the relaxation is induced by temperature (linear response) or by mechanical strain (nonlinear response). Consistent with the well-known Lindemann criterion for melting of crystals, such a unified scenario offers a common structural basis for the thermally activated and strain-induced glass-liquid transition. Our results thus broaden the application range of the Lindemann stability criterion.

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