

Mechanical relaxation in supercooled liquids of bulk metallic glasses

Feature Article

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Received 27 August 2010, revised 20 October 2010, accepted 21 October 2010

Published online 19 November 2010

Keywords glass transition, metallic glasses, relaxation, supercooled liquids

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We report the mechanical relaxation behaviors in typical supercooled liquids of bulk metallic glasses (BMGs). The metallic supercooled liquids are ideal systems for studying intrinsic motions of glass-former supercooled liquids because their structure is close to the simple “dense random packing of spheres” model. We show that the primary relaxation in the frequency domain is dissipative and can be described by the empirical Kohlrausch–Williams–Watts function, and the temperature dependence of the primary relaxation time has the Vogel–Fulcher–Tamman form. Beyond the primary relaxation,

an excess wing is found on the high-frequency tail of the primary relaxation. A corresponding shoulder is exhibited at a given frequency in the temperature region below the glass-transition temperature. The experimental results confirm that the decoupling between the slow β relaxation and the primary (α) relaxation exists in metallic supercooled liquids. Based on the current models of the glass transition, we demonstrate that the dynamically heterogeneity originates in the heterogeneous microstructure of metallic supercooled liquids, and a picture of the heterogeneous microstructure is provided.

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1 Introduction

1.1 Metallic supercooled liquids Metallic supercooled liquids are ideal systems for studying intrinsic motions in the glass-forming supercooled liquids. Their structure is close to the dense random packing of spheres. Unlike glass-forming supercooled liquids with dense network packing with covalent bonds, such as supercooled liquids of oxide glasses, metallic supercooled liquids are newcomers, and have only recently become experimentally accessible after the discovery of BMGs [1–3]. The first metallic glass ribbon trapped from metallic supercooled liquid by cooling was Au–Si, obtained by Duwez and coworkers in 1960 [4]. The vitrification was processed by the rapid quenching technique at very high rates of 10^5 – 10^6 K/s. In the early 1960s, another important contribution to the subject came from Chen and Turnbull [5]. They illustrated the similarities among metallic glasses, ceramic glasses, and other glasses, and confirm the glass transition in the rapidly quenched Au–Si glasses as well as Pd–Si and Pd–Cu–Si glass-forming alloys. The result verified for first time that metallic SLs can be reproduced on the experimental timescale. In the early 1970s the field of metallic glasses had a momentum [6]. In this period, the suction-casting

method was developed and used to form ternary Pd–Cu–Si glass rods with millimeter diameter with much lower cooling rates in the range of 10^3 K/s [7]. The technique has lower cooling rates in the range of 10^3 K/s. At beginning of the 1980s, the boron oxide fluxing method was developed to dissolve/remove heterogeneous nucleates from metallic melts [8, 9]. The treatment significantly improves the glass-forming ability of the metallic Pd–Cu–Si alloys, and glassy ingots of centimeter in size were formed with cooling rates of about 10 K/s.

In the late 1980s, Inoue’s group discovered rare-earth rich alloys such as La–Al–Cu [10] with exceptional glass-forming ability. By casting the alloys into copper molds, the fully glassy rods and bars in the dimension of several millimeters were formed. Thereafter, similar quaternary and quinary alloys were developed to be formed into glasses at cooling rates of less than 10 K/s. Their casting thicknesses reached 1 cm [11]. Similar families of alloys with rare-earth metals partially replaced by the alkali-earth metal, *e.g.*, Mg-based glasses, were also found [12, 13]. At the same time a family of multicomponent Zr-based glasses was produced [14, 15]. These multicomponent glass-forming alloys illustrates that metallic glass formers with good glass-

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forming ability are ubiquitous. In 1993, Johnson's group developed a new ZrTiCuNiBe glass-forming system. Compared to that in conventional metallic SLs, the crystallization process of the metallic SL is astonishing slow [16, 17]. The metallic glassy samples with a minimum dimension larger than 10 mm can be cast at low cooling rates (< 10 K/s). The development of bulk metallic glass (BMG) former affirms that metallic SLs of BMG formers have a high stability against crystallization through a careful selection of composition. The stability of metallic SLs of BMG formers can approach that of conventional oxide glass formers.

Without the complex intramolecular effect, metallic liquids of BMG formers offer an opportunity to understand the complex properties in glass-forming liquids. Quasielastic neutron-scattering experiments exhibited that at high temperatures the structural relaxation of the metallic liquids is similar as those in nonmetallic viscous liquid [18, 19] and can be described with the mode-coupling theory in which the relaxation will separate into multiple processes at a crossover temperature T_C (about $1.2 T_g$). Li et al. [20] observed that certain local atomic motion in $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ undercooled liquid has an obvious change at its crossover range. These results showed that metallic supercooled liquids may have different relaxation behaviors from those above T_C . The deeply undercooled metallic liquids can permit far more extensive investigation of the temperature dependence of the Newtonian viscosity. Data on viscosity over about 15 orders of magnitude has been obtained [21]. They can be fitted well by the Vogel–Fulcher–Tamman (VFT) expression: $\eta = \eta_0 \exp[B/(T - T_0)]$ with VFT temperature T_0 and B ($D = B/T_0$, referred to as the fragility parameter) [22–24]. According to the Angell plot [25, 26], the supercooled liquids of BMG formers are relatively strong.

1.2 Glass transition In 1995, the Science magazine ranks the glass transition to be the sixth major physical question in the 21st century [27]. However, people outside the glass-transition community have difficulty in seeing exactly what the glass-transition problems are. Even insiders split into groups over which question could be the most important for slow dynamics in cold liquids. Some theorists even think it may be impossible to invent a general theory of liquid dynamics because liquid structures are too diverse. While in spite of the multifarious structural peculiarities that exist in liquids, a general relaxation dynamics, *i.e.*, a general scenario for the glass transition can still be observed [28].

Form a phenomenological point of view, upon cooling a glass can be formed if crystallization processes can be avoided completely. During continued undercooling, the viscosity of glass-forming liquids increases gradually. Below some point glass-forming liquid freezes continuously into a noncrystalline solid. This continuous process is normally termed the glass transition [29]. The glass transition looks similar to a second-order phase transition in the Ehrenfest sense with continuity of volume and entropy, but discontinuous changes of their derivatives [30, 31]. These days most of the scientific focus around the glass

transition is on glass-forming supercooled liquid preceding the glass transition. One major reason is that glass derives from a supercooled liquid. Just as in social sciences or history one must know the past to understand the present.

On a dynamic view, the glass transition is a kinetic process of the glass-former liquids. One universal dynamic feature of the glass-forming liquids is related to the temperature dependence of the viscosity. According to Maxwell's expression: $\tau = \eta/G_\infty$, where G_∞ is the instantaneous shear modulus of the liquid, and is much less temperature dependent than τ and η , the relaxation time τ usually is considered to be proportional to viscosity η . The accumulated experimental data have exhibited that η or τ in most glass-former liquids is of non-Arrhenius temperature dependence [32, 33]. In the original "Angell plot," where the logarithm of the viscosity for a number of viscous liquids is plotted as a function of inverse temperature normalized by the glass-transition temperature T_g [25], the Arrhenius law, only works for a few glass-forming liquids, *e.g.*, pure silica or phosphorus pentoxide. In the vast majority of cases glass-forming liquids show a non-Arrhenius increase in the viscosity upon cooling toward the glass transition. Strongly non-Arrhenius liquids are called "fragile," while those closer to Arrhenius behavior are termed "strong." On the other hand, as is generally assumed, dynamics are dominated by barriers to be overcome by thermal fluctuations, one would expect non-Arrhenius form into $\eta \sim \exp(\Delta E/k_B T)$ [34]. So the activation energy ΔE will increase as the decrease in temperature.

A clue is provided by the extremely large viscosity of glass-forming liquids as they approach the glass transition. For a glass-forming liquid the viscosity is typically of order 10^{12} Pa s just above T_g . The viscosity of glass-forming liquids will be so large that conventional methods for measuring the viscosity completely fail as the temperature is less than the glass-transition temperature. This is due to the fact that a time of about 10^9 s is needed to observe the flow of the viscous liquids at T_g [30]. Therefore, such a system appears absolutely solid, but is still a liquid according to any reasonable scientific definition, as long as it is in thermal equilibrium.

The second universal dynamic feature of the glass-forming liquids is the nonexponential relaxation behavior [35, 36]. When a glass-forming liquid is subjected to a sudden constant thermal, mechanical, or electrical perturbation, there is a relaxation toward steady state. This relaxation is almost always nonexponential. The temporal behavior of the response function $F(t)$ (*e.g.*, the strain in response to a deformation) can often be described by the stretched exponential, or Kohlrausch–Williams–Watts (KWW) function, $F(t) = \sigma(t) - \sigma(\infty) / \sigma(0) - \sigma(\infty) = \exp[-(t/\tau)^\beta]$ ($\beta < 1$), where σ is the measured quantity, τ is a characteristic relaxation time, whose temperature dependence is often non-Arrhenius [37, 38]. In the linear case the perturbation in principle is infinitesimal. Linear perturbations are often studied in the frequency domain where a periodic input results in a periodic output. The ratio between output and

input defines the relevant, complex linear response function. Linear response theory is based on the fluctuation-dissipation theorem, which allows one to calculate the response function from equilibrium fluctuations [30]. An exponential equilibrium ($\beta = 1$) results in the so-called Debye function $\sigma(2\pi f) \propto 1/(1 + i2\pi f\tau_0)$, where f is frequency loaded. It seldom works for glass-forming liquids as temperature is approaching the glass-transition temperature.

For many glass-forming supercooled liquids there is an addition dynamic process, slow β relaxation [39] at higher frequencies in the frequency domain. That is, the loss susceptibility $\sigma(f)$ contains two peaks: primary (α) and slow β peak. The former only appears at temperature above T_g ; the latter can survive below T_g and display Arrhenius behavior. The separation of α - and β relaxations in glass-forming SLs is another problem related to the glass transition. The slow β relaxation was first observed by Johari and Goldstein [39]. Based on kinetic density fluctuations in supercooled liquids, it, referred to as “islands of mobility,” was originally seen to represent local diffusion involving both rotational and translational in loosely packed isolated regions [40]. It is noted that mode-coupling theory can predict the separation of the α and β relaxations [41]. But this universality of the separation in supercooled liquids is now weakened by some facts [42–44]. Many glass-forming supercooled liquids do not show a well-resolved slow β relaxation, but a shoulder termed as an excess wing on the high-frequency side of the α relaxation peak [45–51]. Ngai et al. [46] proposed that the excess wing was just the high-frequency flank of the slow β peak, the low-frequency part of which is fully hidden by the dominant α peak. However, based the Nagel scaling Dixon et al. [42] thought that the excess wing was an intrinsic feature of the α relaxation. There is no consensus on this problem even at a qualitative level.

1.3 Models of glass transition A well-known model for the non-Arrhenius behavior is the free-volume model [52–54]. In the free-volume model, which actually exists in several versions, the excess volume relative to atomic/molecular volume is termed the “free” volume. It is intuitive and crude that the free volume determines the dynamic characteristics of SLs. The contraction of the liquid upon cooling strongly affects the rate of molecular/atomic motion since volume is needed for molecular/atomic rearrangements. Although this quantity obviously decreases upon cooling, it is impossible to measure the free volume rigorously because a molecule/atom does not have a definite volume.

As well as the free-volume model, the entropy model [55] can also predict the non-Arrhenius behavior of SLs. Assuming that molecular/atomic reorientations take place cooperatively, Adam and Gibbs [55] introduced the idea of cooperatively rearranging regions into glass-former liquids. The size of the cooperatively rearranging regions is determined by at least two different configurational states. With another assumption that the activation energy is proportional to the region volume, the model predicts the

non-Arrhenius behavior of SL: $\tau = \tau_0 \exp[C/TS_{\text{conf}}(T)]$. Now, the entropy model is generally regarded as experimentally vindicated. However, the assumptions in this model have been challenged [56]. The predicted identity of the Kauzmann temperature with the temperature where the VFT expression for the viscosity divergence, is questioned [57]. The size of the cooperative rearrangement region in glass-forming supercooled liquids has been found experimentally to be only several nanometers. This is clearly inconsistent with the assumption in the Adam–Gibbs model where cooperative rearrangement region is largely unaffected by its surroundings. Moreover, the configurational entropy identified with the so-called excess entropy, *i.e.*, liquid minus crystal entropy at the given temperature [56, 58], is still questionable.

Besides entropy and volume, a third class of models has been proposed to take energy as the controlling variable [59–65]. In the simplest version as mentioned above, thermal excitation is assumed to take place to a specific barrier energy E_0 . If a process is cooperative, the most thermal energy of a rearranging region is close to its average energy $E(T)$. This implies that $\Delta E(T) \cong E_0 - E(T)$. So as the temperature is lowered, the activation energy increases. However, this model implies linear-response loss peaks these are too broad unless the cooperatively rearranging regions are quite small.

The mode-coupling theory provides a first-principles approach to the glass transition. Starting with Newton's equations of motion and after several nontrivial approximations, the mode-coupling theory ends up with definite experimental predictions [41, 66, 67]. In ideal mode-coupling theory the dynamics are determined by static equilibrium averages. The theory predicts a critical temperature T_C below which there is a nonergodic phase. In fact, T_C is always found to be higher than T_g . There are extensions of mode-coupling theory that take processes activated by thermal energy into account. The extensions broaden the theory's range of applicability to lower temperatures.

Many other ways to predict the non-Arrhenius property of glass-former liquids have been proposed, *e.g.*, the energy-landscape approach [28, 34, 68–70]; models with trivial thermodynamics, but nontrivial dynamics [71–73]; the random first-order transition theory [74, 75]; the entropic barrier hopping theory [76]; and the theory of frustration-limited domains [77]. Most of these models describe that the slowing down in glass-forming liquids is a consequence of an underlying or narrowly avoided phase transition.

Finally, the current-shoving model gives another picture of the dynamic behavior [78]. In the model, viscous glass-forming liquids are to be viewed more as “solids that can flow” than as less-viscous liquids like ambient water. This is due to the fact that a glass-forming liquid close to the T_g has an extremely large viscosity. Most molecular/atomic motion goes into vibrations, just like in a solid. Only very rarely does anything happen in the form of a flow event, a molecular rearrangement. A flow event, like any barrier crossing, happens on a fast timescale (picoseconds) by a very thermal

fluctuation. Similar to what Goldstein emphasized [34], the barrier for a flow event must be considerably larger than the thermal energy [79]. Thus, standard solid-state elasticity theory can be used to calculate the “shoving” work. In an ideal glass-forming liquid system that consists of dense random packing of spheres, such as metallic glass-forming liquids, the shoving work is related to the shear modulus. Since this flow event happens on a fast timescale, the shoving work is proportional to the instantaneous shear modulus, G_∞ . The final expression of the temperature-dependent activation energy in the shoving model is the product of V_c and $G_\infty(T)$. V_c is a characteristic microscopic volume, which is assumed to be temperature independent.

2 Experimental techniques The conventional probes of local structural relaxation, such as dielectric measurement, are not applicable to study atomic motion at microscopic scales in metallic systems. For nuclear magnetic resonance, a difficulty has arisen from the fact that the relevant timescale of atomic motion near T_g is very long compared to the typical nuclear spin-lattice relaxation time in metals. Fortunately, dynamic mechanical analysis (DMA) is a useful and convenient technique to study the relaxation of metallic SLs [80, 81].

The results from dynamic mechanical spectroscopy are usually presented as spectra of real and imaginary parts of the complex elastic modulus $\sigma^* = \sigma' + i\sigma''$. σ can be Young's modulus or shear modulus depended on the measurement type. The complex elastic modulus σ^* can be defined by $F(\omega) = \sigma^* S(\omega)$ with the force $F(\omega)$, and the displacement $S(\omega)$. The real part σ' is the frequency-dependent elastic modulus. The imaginary part σ'' is proportional to the part of F that is out of phase with the displacement with a phase difference of $\pi/2$. It is proportional to the “loss” of energy from the applied force into the sample, therefore denoted as the loss modulus. By DMA, dynamic processes can be detected that involve the displacement of elastic entities. Relaxation processes of such entities occur if they are subjected to a stress changing with time.

In many cases structural relaxation is connected with the stress active processes, *e.g.*, the translational movements in isotropic system or reorientational of elastic entities in a heterogeneous system. In this way, information on the structural relaxation can be gained from the DMA measurements. In a system the translational movements of elastic entities is noninteracting applying a stress field. If we assume that the timescale of the considered relaxation process is clearly separated from those faster and slower processed. It is reasonable to consider that the elastic entities will relax with a rate that is proportional to the distance from their current equilibrium. For the relaxation part of the elastic modulus, $\partial\sigma(t)/\partial t = \sigma_0 - \sigma(t)/\tau$ is deduced. σ_0 is the “static” elastic modulus. Solving the equation above results in an exponential approach of elastic modulus: $\sigma(t) = \sigma_0 + (\sigma_\infty - \sigma_0)\exp(-t/\tau)$. σ_∞ is the instantaneous elastic modulus. The application of a Fourier transformation leads to the following expression

for the frequency-dependent elastic modulus: $\sigma^* = \sigma_\infty + \sigma_0 - \sigma_\infty / (1 + i2\pi f\tau)$.

For the description of the primary relaxation in glass-forming SLs, the assumption of elastic entities with identical relaxation times, relaxing independently from each other, seems unrealistic. Indeed, in most materials the Debye response, the above equation, is not sufficient to describe the experimental results. The loss peaks caused by the primary relaxation (called α peaks) are usually broader and often asymmetric. In dielectric measurements, various modifications of the Debye expression have been proposed to take account of the observed deviations [82], *e.g.*, in the Cole–Davidson (CD) equation [83], $\sigma^* = \sigma_\infty + \sigma_0 - \sigma_\infty / (1 + i2\pi f\tau_{CD})^{\beta_{CD}}$, the addition of the exponent $\beta_{CD} < 1$ takes into account an asymmetric broadening of the loss curves at frequencies above the peak frequency f_p . For $f \gg f_p$ the loss calculated from the above equation follows a power law with an exponent equal to $-\beta_{CD}$.

The finding that in most materials the loss peaks are broadened in comparison with the Debye response is usually ascribed to a distribution of relaxation times. The distribution of relaxation times may arise from the heterogeneity of the material under investigation. The heterogeneity is caused by variations of the local environment of the relaxing entities. An alternative scenario is that of a homogeneous nonexponential response of the relaxing entities in the time domain. Usually, the nonexponentiality is taken into account by the so-called stretched exponential or KWW function: $\sigma(t) = \sigma_0 + (\sigma_\infty - \sigma_0)\exp[-(t/\tau_{KWW})^{\beta_{KWW}}]$ with $\beta_{KWW} < 1$. The KWW equation, in the beginning purely a phenomenological description, has been theoretically derived in a variety of models [84].

3 Results and discussions

3.1 Non-Arrhenius behavior Like other glass-forming supercooled liquids, the non-Arrhenius behavior of metallic supercooled liquids is shown first by the temperature of the viscosity. The stability of BMG-forming liquids in the undercooled region has permitted more extensive investigation of the temperature dependence of the viscosity [85, 86]. Their undercooling is deeper than possible previously [87–89]. A variety of techniques has been used to measure viscosity over about 15 orders of magnitude from the equilibrium melt down to the deeply undercooled range near T_g [1]. Figure 1 exhibits the viscosity data Vit4 [16] obtained by the parallel-plate rheometry [90]. The data are well fitted by the VFT expression $\eta = \eta_0 \exp[DT_0/(T - T_0)]$. The parameters reduced from best fit are $T_0 = 372$ K and $D = 22.7$. Following Angell's fragility [25], the BMG-forming supercooled liquid is rather strong.

Figure 2 shows the apparent complex Young's modulus varying with temperature in the available metallic supercooled liquid region of a Vit4 alloy. In the temperature region the storage Young's modulus E' has a tendency to drop to zero as temperature increases from 643 to 715 K. At a given temperature, it is found that E' is dependent on the frequency

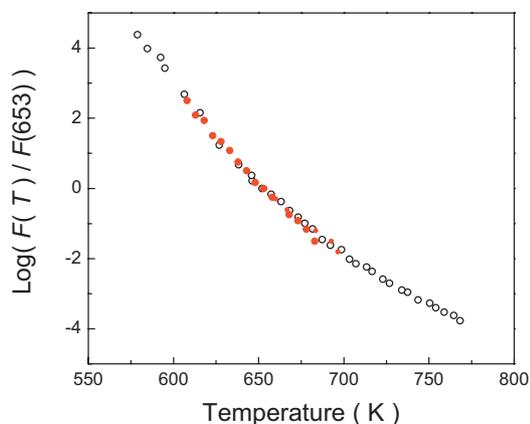


Figure 1 (online colour at: www.pss-a.com) Summary of viscosity data on Vit4 taken using a variety of experimental methods (digitized from Ref. [90]); the solid circles represent the frequency dependence of loss peak temperature of the mechanical relaxation.

loaded. An obvious liquid manner appears since E' moves toward zero as the measured frequency approaches zero. A solid behavior is exhibited as the observed timescale is short enough. E' tends to approach a nonzero value when frequency increases. Correspondingly, a unique broad loss Young's modulus E'' peak can be found for each frequency. As the frequency increases, the E'' peak shifts to higher temperature. A unique E'' peak at a given frequency indicates that only the primary relaxation of the metallic supercooled liquid can be observed. The primary relaxation is the dominating relaxation process in the metallic supercooled-liquid region.

Compared to the viscosity, the mechanical relaxation can provide a clear clue to understand the origin of the non-Arrhenius behavior in metallic supercooled liquids. The relation between the E'' peak frequency f_p and the E'' peak

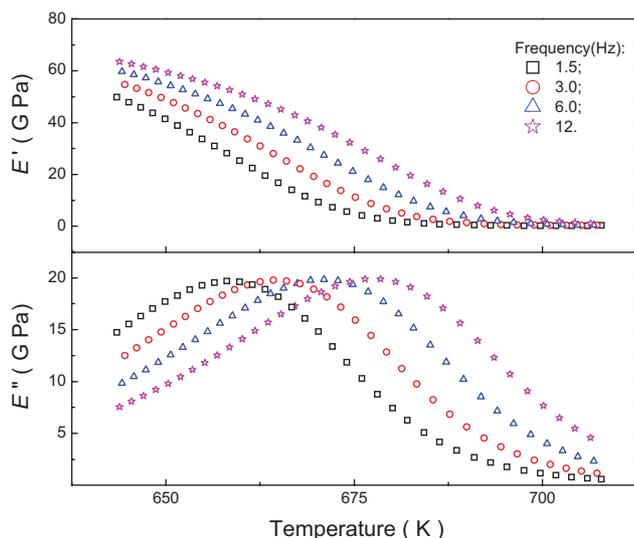


Figure 2 (online colour at: www.pss-a.com) The complex Young's elastic modulus ($E^* = E' + iE''$) determined by DMA during the upscanning at 3 K/min for Vit4.

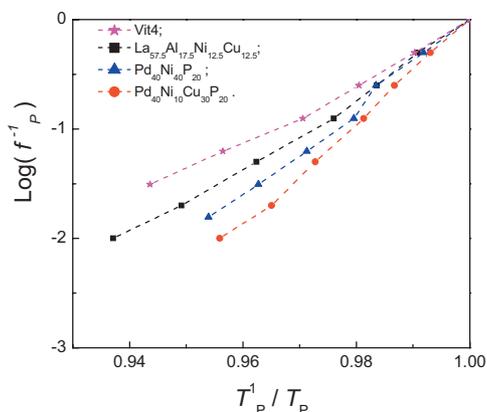


Figure 3 (online colour at: www.pss-a.com) The loss-peak frequency dependence of the reduced loss-peak temperature T_p^1/T_p for different BMGs obtained during the upscanning at 3 K/min by DMA.

temperature T_p is informative to characterize the mobility of the metallic supercooled liquid. The E'' peak frequency f_p as a function of the E'' peak temperature T_p is exhibited in Fig. 1. In order to compare the temperature dependence of the viscosity, reduced $f_p^{-1}(T_p)/f_p^{-1}(653)$ versus reduced $653/T_p$ are plotted. It is found that the viscosity and DMA data are merged into one curve. This means the primary relaxation observed by DMA has an intrinsic connection with the viscosity. At least, the temperature dependence of the viscosity has same activation energy as that of the primary relaxation. As for the form of the temperature dependence of viscosity, the relationship between f_p and T_p is also described well by the VFT expression: $f_{max} = f_0 \exp(-B/(T-T_0))$ [27]. The values of f_0 , B , and T_0 derived from the best fit are 1.2×10^{13} Hz, 9749 K, and 352 K, respectively. Contrary to the prefatory, η_0 , in viscosity form, one can find that the value of f_0 has a physically reasonable meaning. It is close to the typical attempt frequency.

Figure 3 exhibits the T_p dependence of the f_p in four metallic supercooled liquids. The T_p is reduced by the T_p^1 measured at 1 Hz. The error of the T_p is less than 0.5 K, that is dependent on the probing time and the heating rate in the DMA measurement. All data can be fitted well by the VFT equation: $f_p = f_p^0 \exp[-B/(T_p - T_0)]$. The parameters of B , T_0 , and f_0 obtained from the best fit by the VFT equation are listed in Table 1. It is found that all of the prefatory f_p^0 for all of these metallic SLs is close to a typical attempt frequency, i.e., 10^{13} Hz.

At first glance, it may look a puzzle. Dynamics on a timescale differing by about 12 orders of magnitude from the attempt frequency to the f_p of the primary relaxation frequency in metallic supercooled liquid could be connected. In fact, the connection is related to the origin of the non-Arrhenius behavior of the primary relaxation in the metallic supercooled liquids. It is well known that the structure of metallic supercooled liquids is usually considered as a dense random parking of hard/soft spheres. The vibrations of spheres in the metallic system do not result in any compression of the surroundings, and so has no contribution

Table 1 The parameters in $f = f_0 \exp[B/T - T_0]$ for various metallic glass-forming systems. The glass-transition temperature T_g is measured by differential scanning calorimeter at a heating of 20 K/min.

BMGs	f_0 (Hz)	B (K)	T_0 (K)	fragility index m	T_g (K)
Vit4	4.3×10^{14}	10 200.0	352 ± 10	34.2	640
La _{57.5} Al _{17.5} Ni _{12.5} Cu _{12.5}	3.98×10^{14}	6170.6	270.9 ± 10	43.3	435
Pd ₄₀ Ni ₄₀ P ₂₀	1.6×10^{13}	5380.7	419 ± 10	52.3	580
Pd ₄₀ Ni ₁₀ Cu ₃₀ P ₂₀	5.6×10^{12}	4062.5	442 ± 10	61.4	570

to the mechanical relaxation. The mechanical relaxation takes place only when atomic translational motions in metallic supercooled liquids take place. As for the description of the shoving model of the glass transition, the atomic translational motions are referred to as “flow events.” The short timescale (picosecond scale) is much less than that of the barrier transitions. Properties on the long timescale may very well be relevant since the actual determining barrier height sets the clock for the long timescale. The barrier height or the activation energy for atomic translational motion in metallic supercooled liquids is determined mainly by the instantaneous shear modulus, G_∞ . The temperature dependence of G_∞ is responsible for the non-Arrhenius behavior. Here, unfortunately, the temperature dependence of G_∞ of the metallic supercooled liquids cannot be measured directly. But the temperature dependence of G_∞ in some other glass-forming SLs has been obtained and confirmed the shoving model [91, 92]. So, the prefatory f_p^0 in the VFT equation for the primary relaxation determined by DMA offers a clear clue to understand the non-Arrhenius behavior of metallic supercooled liquids. The non-Arrhenius behavior arises from the translational atomic motions in systems with dense random packing structure.

3.2 Nonexponential behavior Figure 4 presents the E' and E'' spectra of Vit4 supercooled liquid in the frequency domain. The spectra are measured isothermally at different temperatures within its available supercooled liquid region (from 608 to 688 K). In order to avoid partial crystallization during measurement, the measuring time was controlled precisely, especially at temperatures above 658 K. It is found that the experimental frequency range ($10^{-2} \leq f \leq 200$ Hz) is effective to determine almost the whole spectra of the primary relaxation, and to reveal how the relaxation evolves as the temperature T increases up to the onset temperature of crystallization.

All spectra of E'' representing the primary relaxation are dominated by a single peak shifting through the frequency axis with temperature. Empirically, the primary relaxation is often described with the Fourier transform of the KWW function. The solid lines are drawn with the KWW equation. The fit yields a better representation in the peak region, but obvious departures are found for the higher-frequency data. With the best fitting, the value of β_{KWW} is about 0.5 in the temperature range of 688–608 K. Besides that, a departure at the high-frequency flank (*i.e.*, the excess wing) can be found. The departure becomes more obvious with decreasing temperature. Similar phenomena can be found in

Pd₄₀Ni₁₀Cu₃₀P₂₀ metallic supercooled liquid. The value of β_{KWW} is about 0.45 in the temperature range of 563–593 K. This departure has been found to be common for the primary relaxation of glass-forming supercooled liquids without obvious slow β peak when the temperature approaches T_g . The relationship between m and β_{KWW} in two metallic supercooled liquids does not obey qualitatively the empirical correlation [93]. That is, the non-Debye behavior of the α relaxation (β_{KWW}) and the fragility m is summarized by a function, $m = m_0 - s\beta_{KWW}$, with $m_0 = 250 \pm 30$ and $s = 320$.

Figure 5 represents master curves of the loss Young’s modulus versus the frequency for the above two metallic supercooled liquids. On the low-frequency side of the loss peak, these two systems behave in almost the same way, but they differ significantly at high frequencies. After bifurcation at about 10 frequencies, the spectra of Pd₄₀Ni₁₀Cu₃₀P₂₀ metallic supercooled liquid possess a larger value of normalized E'' and the difference tends to increase with frequency. The master curves display that the characteristics of primary relaxation are different in the two metallic SLs. But both of them obey the time–temperature superposition.

The time–temperature superposition has been long-standing considered as an important characteristic of α relaxation when T approaches T_g [94]. However, more and

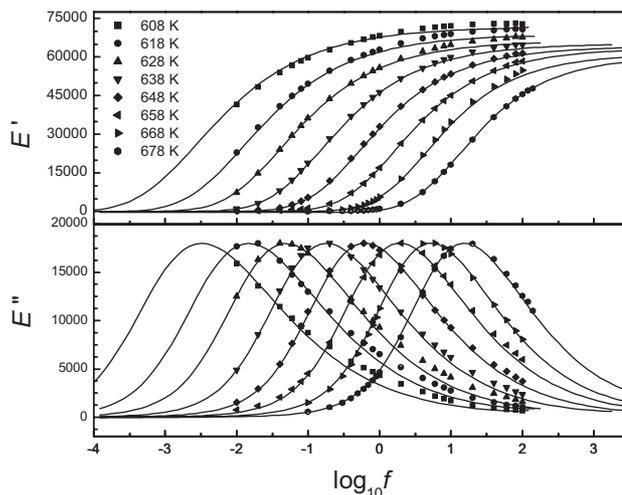


Figure 4 The frequency dependence of the storage and loss Young’s moduli of metallic Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni₁₀Be_{27.5} supercooled liquid determined isothermally by DMA at different temperatures. The solid lines are the fitting curves obtained by the KWW equation.

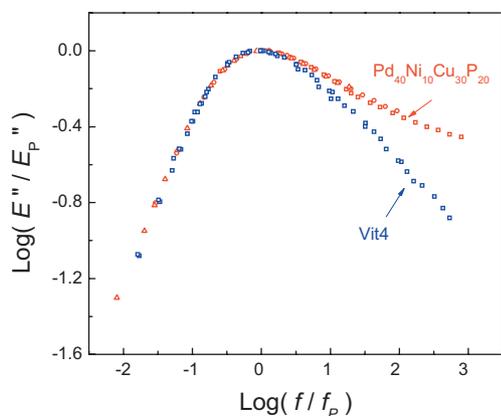


Figure 5 (online colour at: www.pss-a.com) Master curves for Vit4 and Pd₄₀Ni₁₀Cu₃₀P₂₀ metallic supercooled liquids of the mechanical relaxation measured by DMA. Logarithmic scales are chosen for the reduced E''/E_p'' versus f/f_p .

more systems were found not to obey the time–temperature superposition as the experimental accuracy increased and the frequency ranges widened. A common characteristic of the system invalidating time–temperature superposition is that the slope of the relaxation curve below the peak usually is almost T independent, but the slope of the relaxation curve at higher frequency at the peak frequency increases with increasing temperature [95]. These violations can be explained as due to interference from an additional minor relaxation process, namely the β relaxation often found at frequencies higher than those of the dominant α relaxation.

For the relaxation of supercooled liquids without an obvious slow β peak, Nagel and coworkers [42] found an appropriate scaling of the axes to collapse the E'' – f curves, including the peak and excess wing, for different materials onto one master curve. Figure 6 shows a plot of $w^{-1}\log_{10}(E''f_p/\Delta Ef)$ versus $w^{-1}(1+w^{-1})\log_{10}(ff_p)$ [here, the half-maximum width w normalized by a Debye relaxation (1.14 decades), $\Delta E \cong E_\infty$ the relaxation modulus in the high-frequency limit] for five metallic supercooled liquids. The scaling form successfully collapses the loss-modulus data for all temperatures and frequencies onto a single line for all metallic supercooled liquids. In contrast to Ref. [42], the data of metallic supercooled liquids show obvious frequency-dependent behavior. This is because the data of metallic supercooled liquids have to be described by $E'' \sim f^a (f \ll f_p)$ with $a = 0.91$, while the frequency-independent behavior requires $a \cong 1$. Similar result can also be observed in some low molecular weight glass-forming liquids [96]. The solid line represents the KWW curve with $\beta_{\text{KWW}} = 0.7$. It is interesting to find that the solid line can fit well the collapsed plots for $f > f_p$. This means that the different slopes of the high-frequency tails of the relaxation can be scaled by the scaling with the half-maximum width alone. Schoenhals et al. [96] concluded that the half-maximum width alone was insufficient to describe the shape of the relaxation curve, because the width does not contain the information of the slopes of the low- and high-frequency

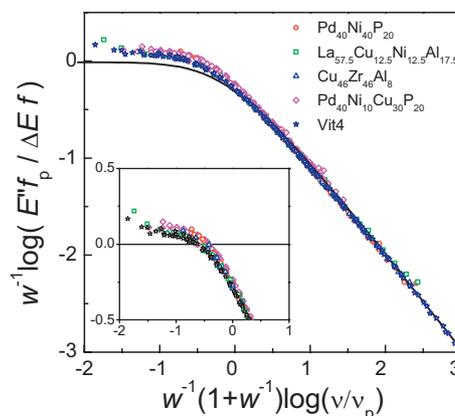


Figure 6 (online colour at: www.pss-a.com) Frequency-dependent E'' for Vit4, Pd₄₀Ni₁₀Cu₃₀P₂₀, Cu₄₆Zr₄₆Al₈, La_{57.5}Al_{17.5}Ni_{12.5}Cu_{12.5} and Pd₄₀Ni₁₀P₂₀ at a temperature in their SL region, scaled according to Nagel and coworkers [42]. w denotes the half-width maximum of the loss peaks normalized to that of a Debye peak, f_p is the α peak frequency and ΔE the relaxation strength.

tails of the relaxation. Until now, no commonly accepted theoretical models can explain this peculiar shape of the relaxation curve.

The nature of the nonexponential primary relaxation has been discussed over many decades [97]. No consensus can exist on ideas whether relaxation occurs exponentially in each spatial domain or intrinsically nonexponential relaxation function in a homogeneous system. The finding of the nonexponential primary relaxation measured by DMA in the metallic supercooled liquids tends to support the former idea. Different from the former idea, the mechanical relaxation is related to the single atomic translational motions, not spatial domain. This is due to the fact that the primary relaxation arises from single atomic translational motions in metallic viscous liquids. The spatial heterogeneity of atoms on the short range is obvious in metallic supercooled liquids.

In the above simple picture, despite the presence of some dynamic averaging, the response function can be viewed to a good approximation as arising from a relaxation time distribution $P(\tau)$ in $\phi(t) = \int e^{-t/\tau} P(\tau) d\tau$ [98]. The relaxation-time distribution arises from the different random atomic position. This will resemble a KWW formula with the β parameter determined by the explicit form of $P(\tau)$, largely by the breadth of the distribution. To find the β value, an explicit distribution of activation energy based on a dynamically fluctuating disorder packing system with high density is needed. To set the stage, a simple assumption should be made: the distribution of the relaxation times is Gaussian resulting from small fluctuations. This approximation already yields a qualitative (but not quantitative) function of β . Thus, the time correlation function can be rewritten as $\phi(t) = \int e^{-t/\tau(\Delta E)} P(\Delta E) d\Delta E$. Here, $\tau(\Delta E) = \tau_0 \exp(\Delta E/k_B T)$. $P(\Delta E)$ is Gaussian. The relaxation function is not precisely a stretched exponential, but is well fit by one with a β value given by $\beta = \left[1 + (\delta E/k_B T)^2\right]^{-1/2}$ [99, 100].

δE is the width of the Gaussian distribution $P(\Delta E) = 1/\sqrt{2\pi\delta E^2}\exp[-(\Delta E - \Delta E_0)^2/2\delta E^2]$. Clearly, δE reduced by thermal activation $k_B T$ determines the value of value of β . This can explain the departure of m and β_{KWW} in two metallic SLs from the empirical correlation since m is determined by the temperature of the averaged activation energy ΔE , while β_{KWW} is dependent on δE reduced by thermal activation $k_B T$. There is no intrinsic connection between m and β_{KWW} .

3.3 Decoupling of relaxation Typically, the viscosity as a function of temperature and the trace of the dynamic glass transition in the Arrhenius diagram consists of three parts [27]. A high-temperature process (a process) exists in the undercooled liquid at high temperature (below melting points), and a cooperative process (α process) appears in a supercooled liquid at low temperature (close to the glass-transition temperature T_g). The transition from a to α is called the crossover region that was first collected for polymers [101]. Besides a and α relaxation, in the Arrhenius diagram of dielectric, mechanical, and other traces for polymers a third process (slow β) is usually exhibited in the supercooled-liquid region below the crossover.

Without the complex intramolecular effect, the observation of the slow β relaxation in metallic glass-forming materials can offer an opportunity to affirm the universality and understand the nature of the slow β relaxation. The measurements of the DMA for Vit4 alloys were processed at a frequency of 2 Hz during an upscanning at 3 K/min. Figure 7 shows the apparent complex shear modulus change with the temperature for two samples. One is the as-cast sample formed by fast quenching at a rate of 100 K/s. The other is that cooled from its supercooled liquid region at 3 K/min without crystallization. The storage E' begins to drop for the two samples when the temperature increases from 625 to 643 K, even though the temperature dependence of the E' is a little different. In this temperature region the calorimetrical glass transition takes place. The difference in E' is related to the different glassy states for the two samples. In the supercooled-liquid region (above about 643 K), the E' is close to zero.

The inset of Fig. 7a shows the enlarged part of the E' in the glassy temperature region. At low temperature, the E' of the sample cooled at 3 K/min is larger than that of the as-cast sample, and is almost independent of the temperature. It begins to decrease at about 550 K when temperature increases. The decrease in the E' is much smaller than that taking place at the glass-transition temperature. On the contrary, the E' of the as-cast sample increases as the temperature increases from 525 K. The increase represents the physical aging taking place during heating. In Fig. 7b the loss E'' contains a peak around 653 K in the supercooled-liquid region. The position of the peak is the same for the two samples within the experimental error. Obviously, the peak arises from the primary relaxation of the metallic SL. Besides

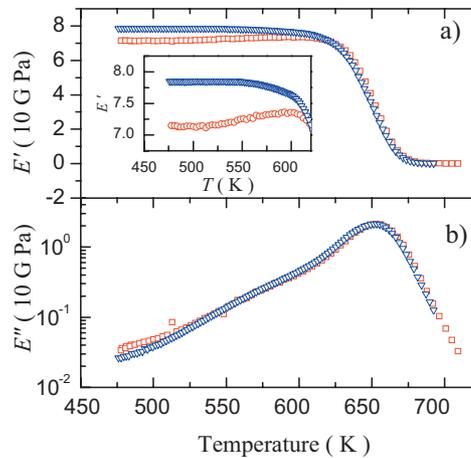


Figure 7 (online colour at: www.pss-a.com) (a) The temperature dependence of the storage Young's modulus E' for the as-cast Vit4 sample (\square) and Vit4 sample with the forming cooling rate of 3 K/min (∇). Inset shows the enlarged part in glassy region; (b) the temperature dependence of the loss shear modulus E'' .

the peak, at lower temperature a shoulder is shown in the E'' curves. The shoulder in the sample formed by the cooling at 3 K/min is accompanied with the decrease in the E' , indicating that an intrinsic relaxation process exists in the glassy region.

The shoulder indicates that the metallic glassy system has the slow β relaxation. This is due to two reasons. One is that the shoulder appears in the temperature region just below T_g . This is consistent with the fact that the slow β relaxation has a lower activation energy than the primary relaxation process. In the temperature domain, it only appears at lower temperature in comparison with the primary relaxation. Another reason is that the shoulder is an intrinsic process in glass that is accompanied by the decrease in the storage modulus. No obvious peak related to the β relaxation is due to the metallic glass system with a rather strong fragile SL. The existence of the slow β relaxation in metallic systems is universal. Figure 8 shows the reduced loss modulus E''/E''_p of the six BMG systems in the temperature domain measured at 1 Hz at the heating rate of 3 K/min [102]. E''_p is the loss modulus at the peak, the temperature T is also scaled by the peak temperature T''_p . The values of T''_p are 652 ± 1 , 675 ± 1 , 728 ± 1 , 580 ± 1 , 596 ± 1 , and 443 ± 1 K for Vit4, $Zr_{65}Cu_{15}Ni_{10}Al_{10}$, $Cu_{46}Zr_{46}Al_8$, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, $Pd_{40}Ni_{40}P_{20}$, and $La_{57.5}Cu_{12.5}Ni_{12.5}Al_{17.5}$, respectively. Common characteristics can be found in the temperature dependence of the E'' curves. That is, all these curves can be divided into three regions. Region I is the low-temperature range where E'' is nearly independent of temperature. Region II has a characteristic shoulder that is found in the glassy state. Such a shoulder is related to the slow β relaxation. Region III is the SL region where a primary relaxation peak can be found.

Therefore, based on the DMA measurement the dynamic glass transition of the metallic glass-forming system in the Arrhenius diagram can be established. Here, we choose the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ metallic system since its SL is rather fragile

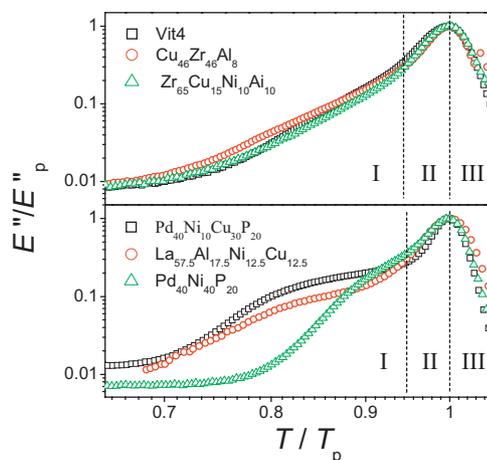


Figure 8 (online colour at: www.pss-a.com) The temperature dependence of reduced loss modulus E''/E_p'' measured by DMA at frequency of 1 Hz during the upscanning at 3 K/min for different BMGs.

among the metallic glass-forming systems. Its slow β process is more obvious in the loss E'' curves (see Fig. 8). The temperature dependence of the E'' peak in $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ supercooled liquid region represents the α relaxation time change in temperature [103]. Figure 9 plots the values of f_{\max} as a function of the temperature T_{\max} at the E'' peak. The relationship between f_{\max} and T_{\max} is described well by the VFT expression: $f_{\max} = f_0 \exp(-B/T_{\max} - T_0)$. The values of f_0 , B , and T_0 are 9.13×10^{12} Hz, 4940.86 K, and 413.24 K, respectively. Since the α relaxation is nonexponential in form, its dispersion zone defined by the full width at half-maximum (FWHM) in $\log_{10} f$ is about 2.4 ($1.144/\beta_{\text{KWW}}$) [27]. The dispersion zone is exhibited as red dashed lines. On the other hand, the temperature dependence of the slow β relaxation time is an Arrhenius process. With the shoulder shifting with the frequency loaded, the temperature dependence of the peak frequency f_{\max}^{β} for the slow β relaxation has the form as following: $f_{\max}^{\beta} = 2.56 \times 10^{14} \exp(-135970/kT_{\max}^{\beta})$. The slow β relaxation dispersion zone is determined by the estimation of the β_{KWW} (around 0.4). In the metallic SL region the α relaxation at the higher frequency overlaps the slow β relaxation at lower frequency. No obvious slow β relaxation E'' peak in the supercooled-liquid region is due to the limit of the DMA measurements. Prior to the crossover temperature (695 ± 30) [104], the slow β relaxation merges into the α relaxation.

4 Summary The development of BMGs affirms that through a careful selection of composition the highly stable metallic supercooled liquids can be obtained. The stability against the crystallization in supercooled liquids of BMGs approaching that of the conventional oxide glasses offers wide temperature and time windows for investigation of the dynamic characteristics in metallic supercooled liquids. Since the microstructure of BMGs represents one of the simplest microstructures among glass-forming systems, the studies of the dynamic behaviors in BMGs, in particularly

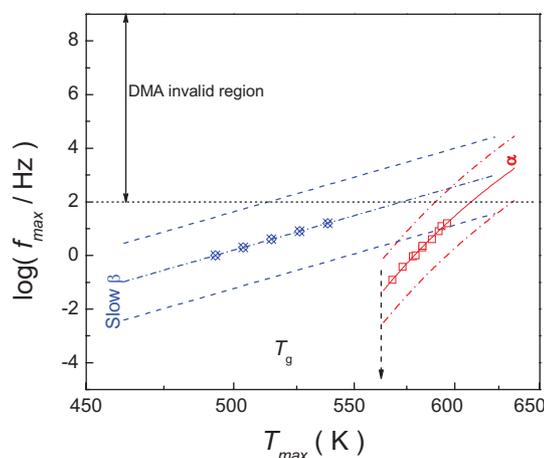


Figure 9 (online colour at: www.pss-a.com) The mobility–temperature Arrhenius diagram of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ BMG-forming supercooled liquid on the base of the DMA measurements. The red empty squares represent the α relaxation peaks changing with temperature, and the corresponding red dashed lines exhibit the FWHM; the blue empty circle plots show the underlying slow β relaxation peaks shifting in temperature that was deduced from the shoulder of E'' appearing at temperature below T_g (see Ref. [103]), and the corresponding blue dashed lines illustrate the position of its FWHM. T_g is about 563 K measured by DSC during upscanning at 20 K/min.

their supercooled liquids, are useful to understand the complicated glass transition. DMA is an effective tool to observe the mechanical relaxation in metallic supercooled liquids, and allow us to obtain spectra of the complex elastic modulus of metallic supercooled liquids. In the presented elastic modulus spectra of six BMG glass formers, two different contributions can be clearly distinguished: the α peak and the excess wing or shoulder. The DMA measurements provide the possibility to follow the development of the two features, starting from the glass region, near T_g , up to temperatures in the supercooled liquid.

Most theoretical approaches of the glass transition concentrate on the description of the α relaxation time. The non-Arrhenius behavior of the α relaxation in BMG SLs can be presented and clarified by DMA measurements. Contrary to the viscosity, the prefatory f_p^0 in the VFT equation of the α relaxation has a physically reasonable meaning, a typical attempt frequency 10^{13} Hz. The mechanism of the non-Arrhenius behavior is similar to the explanation of the shoving model. That is, the non-Arrhenius process arises from the temperature dependence of the large activation energy of flow events in a viscous supercooled liquid. A flow event, like any barrier crossing, happens on a fast timescale (picoseconds) by thermal fluctuation. The thermal fluctuation with the large activation energy results in a behavior as a solid during a flow event. The long time between two flow events arising from the thermal fluctuation accounts for the large viscosity of supercooled liquids. In metallic supercooled liquids the flow events are atomic translational motions.

The nonexponential behavior of two prototypical metallic supercooled liquids is confirmed. The supercooled liquids of Vit4 and Pd₄₀Ni₁₀Cu₃₀P₂₀ BMG have a broad loss E'' spectra in the frequency domain. It departs clearly from the Debye relaxation behavior. The fragile metallic supercooled liquid has broader loss E'' spectra than the strong metallic supercooled liquid. It is found that the origin of the nonexponential behavior is same as that of the non-Arrhenius. That is related to the atomic translational motion in dense random sphere packing. According to the ideas in the microscopic theory of heterogeneity of supercooled liquids, the characteristic parameter β_{KWW} is connected qualitatively with the averaged breadth of the relaxation time distribution δE normalized by $k_B T$. At the same time, an excess wing is found. The excess wing can collapse onto one master curve. The excess wing is not intimately related to the α relaxation, but due to the corroboration of the independent β relaxation process with the α relaxation.

The universality of the β relaxation in glass-forming systems is confirmed by the DMA measurements of BMG, which provides a deep understanding of the physical nature of the slow β relaxation. Based on the microstructure heterogeneity models of the liquid–glass transition, the decoupling of the relaxation in metallic supercooled liquids represents the intrinsic microstructure heterogeneity of metallic supercooled liquids. Similar to the normal metallic alloys composed of polycrystalline grains and boundaries between grains, the microstructure of BMG is made up by high-density regions (metastable islands) and low-density region (boundaries between metastable islands). The translational diffusion of the atoms in the low-density region represents the slow β relaxation. Since the distribution of the atom position in the low-density region is wider than that in high-density region, the loss E'' peak related to the slow β relaxation in DMA spectra is wider than that representing the α relaxation. On the contrary, the height of the loss E'' peak related to the slow β relaxation is much lower than that representing the α relaxation. This is due to the fact that the metastable islands is dominative in the microstructure of supercooled liquids. Moreover, since the BMG forming supercooled liquids are rather strong supercooled liquids, in the view of an energy landscape, strong landscapes consist of single “megabasin.” It can be understood that the activation energy for atomic translational motions in low-density regions is not much different from that in the high-density region. Therefore, the slow β relaxation is coupled with the primary relaxation. The slow β relaxation is only observed as an excess wing at the high-frequency tail in the frequency domain. In the temperature domain the slow β relaxation appears in the low-temperature tail of the primary relaxation.

Acknowledgements The financial support of the Natural Science foundation of China (No. 50671118 and 50921091) is appreciated.

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