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# A Direct Link between the Fragile-to-Strong Transition and Relaxation in Supercooled Liquids

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ABSTRACT: It is known that both the fragile-to-strong (F−S) transition and relaxation processes occur in numerous supercooled liquids upon cooling toward the glass transition temperature. The key question is whether and how these two dynamic processes are correlated. Here, we show a direct link between the two processes for both metallic glass-forming liquids (MGFLs) with different fragilities and also for nonmetallic glass-forming liquids. By comparing the F−S transition extent parameter f with the parameter r that characterizes the competition between the α and the slow β relaxations, we have discovered a negative exponential connection between the two parameters of supercooled liquids. The finding indicates that the slow β relaxation plays a dominant role in the F−S transition. This work provides new insight into the microscopic mechanism of the F−S transition and creates a strong basis for predicting whether and to what extent the F−S transition occurs in supercooled liquids.

SECTION: Kinetics and Dynamics
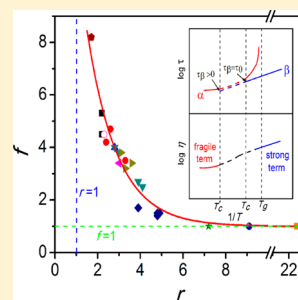
It has been observed that many glass-forming liquids (GFLs), such as water and silica,[1,2] are transformed from fragile to strong liquids in the supercooled region upon cooling. This is the so-called fragile-to-strong (F−S) transition. Since its discovery by Ito et al. in 1999,[1] the F−S transition has attracted considerable interests of researchers.[3−5] However, due to the intervention of crystallization in the supercooled liquid region, it is extremely difficult to obtain dynamic data of the F−S transition for poor glass formers, for example, metallic systems. Despite this, experimental[6,7] and theoretical results[8,9] regarding the dynamics of a large number of metallic glass-forming liquids (MGFLs) have been achieved, which imply that the F−S transition might be a general dynamic phenomenon of MGFLs.[6−10] To quantify the extent of the F−S transition, the transition extent parameter f has been introduced, which is the ratio m'/m, where m' is obtained by extrapolating the viscosity data above liquidus temperature to the glass transition temperature (T_g) via the Mauro−Yue−Ellison−Gupta−Allan (MYEGA) equation,[11] and m is the fragility index of the supercooled liquid at around T_g.[7−10]

To clarify the microscopic origin of the F−S transition, numerous studies have been carried out both theoretically and experimentally. Jagla has ascribed the F−S transition in water to the competition between two different local structures.[12] According to the two-order parameter model, the F−S transition could be the crossover from a non-glass-forming to a glass-forming branch.[13] Liu et al. have attributed the F−S transition to a transition from a high-density liquid to a low-density liquid.[14] All of these models are based on the idea that two kinds of structures are competing in the supercooled liquids during cooling. Recently, by performing thermodynamic analysis of metallic glasses far from equilibrium, we have further

verified the scenario that the high-temperature (HT) and the low-temperature (LT) clusters in MGFLs are rather different and the competition between them contributes to the abnormal enthalpy changes of supercooled liquids during cooling.[15]

It is worth noting that the F−S transition is accompanied by different relaxation processes in supercooled liquids upon cooling. There are two characteristic structures governing the two relaxation modes in MGFLs: the primary α and the slow β relaxations.[16,17] The primary α relaxation is characterized by the non-Arrhenius temperature dependence, whereas the slow β relaxation is described by the Arrhenius one.[18] There is an inherent competition between the two relaxation modes in MGFLs, and this is elaborated by the coupling model (CM)[19,20] and the Williams−Watts (WW) model,[21,22] as well as being confirmed by both the dynamic-mechanical analysis (DMA)[23,24] and the differential scanning calorimetry (DSC) measurements.[25,26] Another scenario proposed by Tanaka, in which the sole relaxation mode is divided into two relaxation modes (the α and the slow β relaxations) at a critical temperature during cooling, is helpful for understanding the dynamics of supercooled liquids in the framework of relaxation modes.[27]

Because both the F−S transition and relaxation in MGFLs simultaneously occur in supercooled liquids during cooling, we are curious about whether both processes are connected with each other. If they are connected, how do we quantify the correlation between them? Answering these questions is crucial for revealing the microscopic origin of the F−S transition and

Table 1. Characteristic Parameters of 23 GFLs Listed in an Ascending Order of the Fragility Index m

composition	m	m'	f	T_g/K	E_α/kJ	E_β/kJ	r	ref
$Pr_{55}Ni_{25}Al_{20}$	19	156	8.2	484	176.1	104.6	1.7	8, 32
$Gd_{55}Al_{25}Co_{20}$	25	113	4.5	589	281.9	127.3	2.2	8, 33
$Gd_{55}Al_{25}Ni_{10}Co_{10}$	25	133	5.3	579	277.1	125.2	2.2	8, 33
$Sm_{55}Al_{25}Co_{10}Cu_{10}$	27	114	4.2	534	276.0	115.4	2.4	8, 34
$Sm_{50}Al_{30}Co_{20}$	29	136	4.7	586	325.3	126.7	2.6	8, 34
$Ce_{55}Al_{45}$	32	127	4.0	541	331.4	116.9	2.8	8
$Cu_{50}Zr_{50}$	32	127	4.0	664	406.8	143.5	2.8	10
$Al_{87}Co_8Ce_5$	34	114	3.4	558	363.2	120.6	3.0	8, 35
$Cu_{49}Zr_{49}Al_2$	34	129	3.8	674	438.7	145.7	3.0	10
$La_{55}Al_{25}Ni_{15}Cu_5$	34	130	3.8	474	321.9	102.5	3.1	8, 36
$Sm_{55}Al_{25}Co_{10}Ni_{10}$	37	130	3.5	553	391.7	119.5	3.3	8, 34
$La_{55}Al_{25}Ni_{20}$	40	127	3.2	491	362	110	3.3	8, 26, 30
$La_{55}Al_{25}Ni_5Cu_{15}$	40	134	3.4	459	353	99.2	3.6	8, 36
Vit105	41	71	1.7	661	518.8	131.9	3.9	7
$Cu_{48}Zr_{48}Al_4$	44	117	2.7	683	575.3	147.6	3.9	10
Vit106a	50	70	1.4	668	639.4	133.3	4.8	7
Vit106	50	75	1.5	670	641.3	135	4.8	7, 37
Vit101	51	79	1.5	676	660.0	134.9	4.9	7
$Cu_{46}Zr_{46}Al_8$	53	130	2.5	701	711.2	174.1	4.1	10, 23
water	22	98	4.5	165	69.5	32.3	2.2	8
OTP	81		1.0	245	381	53	7.2	31, 38
sorbitol	93		1.0	266	474	51.96	9.1	31, 38
PVC	191		1.0	354	1294	57.5	22.5	31, 38

also for establishing a model describing the F−S transition in the framework of relaxation modes. As an initial attempt, Hedström et al. have proposed the possibility of attributing the F−S transition to the divergence of the α and the local β relaxations.[28] Later, Li et al. found that the critical temperature T_C of the mode coupling theory (close to the diverging temperature of the α and slow β relaxations) coincides with the LT bound of the F−S transition in Zr-based liquids during cooling.[6] We also know that both the F−S transition extent for MGFLs and the contribution of the slow β relaxation to the overall relaxation depend on the fragility index m.[9,29] However, we do not know how relaxation modes directly influence the F−S transition.

In the present work, we explore the correlation between the F−S transition and the relaxation in MGFLs by comparing the transition extent parameter f with the relaxation competition parameter r that is the ratio between the activation energies for the α and the slow β relaxations, respectively (i.e., E_α/E_β). The activation energy depends on the nature of the structure units involved in different relaxation modes.[30,31] In general, E_β is smaller than E_α, indicating that the rather local structures are involved in the slow β relaxation.[30] The closer the E_β and E_α values are, the more comparable the structural units involved in the slow β relaxation and those in the α relaxation are. Therefore, the ratio $r = E_\alpha/E_\beta$ may be regarded as a measure of the competition degree between the α and the slow β relaxations in MGFLs.

Table 1 shows the data of both the F−S transition and relaxation modes for 19 MGFLs. The E_α and E_β values used to calculate the relaxation competition parameter r were obtained by calorimetric or DMA measurements.[23,26,32−38] For $Gd_{55}Al_{25}Co_{20}$, $La_{55}Al_{25}Ni_5Cu_{15}$, and $Sm_{55}Al_{25}Co_{10}Cu_{10}$ MGFLs, the E_β values, which were not available in the literature, were calculated by the empirical equation $E_\beta = (26 \pm 2)RT_g$, where R is the gas constant.[26,30] The fragility index m can be calculated from the equation $m = E_\alpha/(2.303RT_g)$.[39,40]

Inversely, some of the E_α values in Table 1 were calculated from m through the same equation.[29,30,41]

Figure 1 shows the r−m relation for the MGFLs shown in Table 1. It is seen that the relaxation competition parameter r
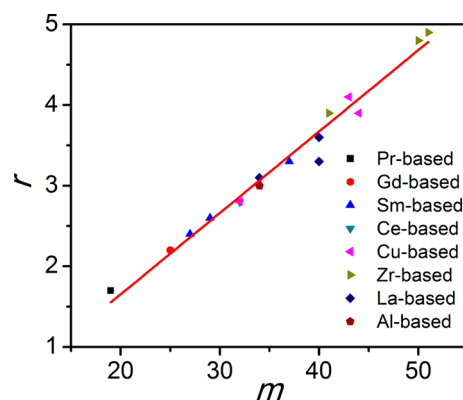

Figure 1. The relaxation competition parameter r as a function of the liquid fragility m for 19 MGFLs. The solid line is the guide for eyes.

increases linearly with an increase in m, that is, a larger fragility index m corresponds to a larger difference between E_α and E_β. This is consistent with the experimental results obtained by DMA,[29] which illustrate the different presentations of the slow β relaxation in MGFLs with different fragilities. Considering that the structure units involved in the α and the slow β relaxations become more comparable in size with a decrease of r, it is difficult to decouple the peak of the slow β relaxation from the α relaxation peak in the DMA measurements for the MGFLs with a small m value. Inversely, the slow β relaxation in the rather fragile MGFLs is manifested as a peak or a shoulder. This tendency has been confirmed by DMA measurements not only in MGFLs[42] but also in nonmetallic GFLs.[31,43,44] For example, for some organic systems such as glycerol, threitol,

xylitol, and sorbitol, it has been found that the width of the α peak increases with a decrease in m, accompanied with the slow β peak disappearing.[44]

The f–r data for the MGFLs (Table 1) are plotted in Figure 2. A negative relationship is found, that is, f increases with a
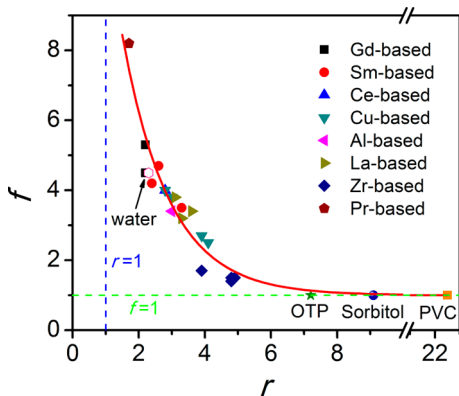

Figure 2. The F−S transition extent parameter f as a function of the relaxation competition parameter r for 19 MGFLs. The solid line is the fit of the equation $f = 21.50 \times \exp(-0.71 \times r) + 1$ to the f–r data for MGFLs collected from the literature (see Table 1). The f–r data of the three nonmetallic systems such as OTP, sorbitol and PVC, which do not exhibit the F−S transition, are also plotted. The data of water (a typical F−S transition liquid) are also included.

decrease in r. This indicates that there is a direct correlation between the extent of the F−S transition and the degree of competition between the α and the slow β relaxations. Theoretically, the MGFLs undergo only a F−S transition upon cooling but never a "strong-to-fragile" transition.[45−47] This means that f is always equal to or larger than 1, as seen in Table 1.[7−10] On the basis of this boundary, the f versus r relation is described by an empirical negative exponential relationship, that is, $f = 21.50 \times \exp(-0.71 \times r) + 1$, with the correlation factor of 0.92, as shown in Figure 2.

As shown in Figure 2, it is seen that the F−S transition disappears, that is, the f value approaches 1 when r is sufficiently large. This may explain why the extent of the F−S transition is quite small or even not observable in many nonmetallic fragile GFLs. To confirm this, we have collected the r values of some small molecule glass formers and polymers from the literature (Table 1), which range from 7.2 to 22.5 and are much larger than those of MGFLs. According to the relation $f = 21.50 \times \exp(-0.71 \times r) + 1$, the f values of these nonmetallic GFLs should be close to the minimum value, that is, slightly larger than or equal to 1. This is exactly the case for experiments because the F−S transition was not observed in these GFLs, that is, $f = 1$.[48,49] Another striking example is water, which has the r value of 2.3 (Table 1). By the negative exponential relation derived from MGFLs, the f value has been predicted to be 5.2 ± 0.42, which is close to the f value of 4.5 derived from viscosity measurements.[8] This implies that the negative exponential relation could be a general feature for GFLs.

In addition, the r values must be equal to or larger than 1 because E_β is always smaller than E_α.[30] This indicates that the maximum extent of the F−S transition is a finite value. According to $f = 21.50 \times \exp(-0.71 \times r) + 1$, the maximum value of f is determined to be around 11.6 at the point of intersection between the fitting exponential curve and the $r = 1$ line in Figure 2. This value (11.6) is close to the theoretically

predicted value (11.7). The latter is the ratio between the theoretical maximum value of $m = 175$ (representing the most fragile liquid)[50] and the theoretical minimum value of $m = 15$ (representing the strongest liquid) predicted from the MYEGA equation.[11] These limiting values of m have been verified by the DSC, DMA, or viscosity measurements on different GFLs.[7−10,32] To the best of our knowledge, only *polyetherimide* shows an m value ($m = 214$) that is higher than the predicted one ($m = 175$).[38]

To clarify the negative relationship in Figure 2, we consider the two possible scenarios proposed by Garwe et al.,[51] which are manifested in Figure 3a and b. Both of them describe the
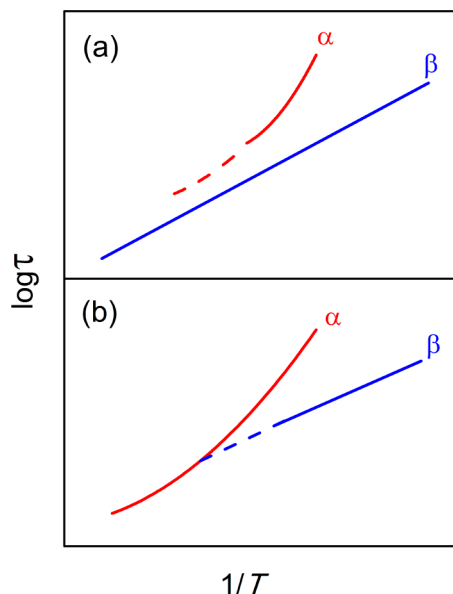

Figure 3. Two scenarios suggested for the merging region in the Arrhenius diagram. τ is the characteristic relaxation time. (a) PnBMA type; (b) PPG type.[51]

splitting or the competition between the α and the slow β relaxation modes in GFLs during cooling. The main differences between the two scenarios lie in the following facts. For the scenario in Figure 3a, the α process dies out at HT, and then, the slow β relaxation is responsible for the HT relaxation. For the scenario in Figure 3b, however, the α relaxation changes continuously in the entire temperature range, and the mechanism of the slow β relaxation changes during cooling at a critical temperature. Figure 4 is a schematic diagram of relaxation modes (a) and the F−S transition (b) based on the theoretical frameworks proposed by other authors.[8,15,18,27] According to Figures 3a and 4, if the F−S transition is mainly attributed to the occurrence of the α relaxation at the embryonic stage during cooling at a critical temperature T_C' (T_C' is denoted as T_A in some case[27]), a larger E_α, along with the constant E_β, that is, a larger r value, would correspond to a larger f. This is contrary to our observation in Figure 2, where f increases monotonously with a decrease in r. In other words, a larger E_β combined with a constant E_α will cause a larger extent of the F−S transition during cooling. This finding agrees well with the scenario in Figure 3b, where the discontinuous change of the slow β relaxation governs the F−S transition. The more contributions from the slow β relaxation during cooling are, the larger the extent of the F−S transition is. From the microstructural aspect, a smaller r or a larger E_β value means

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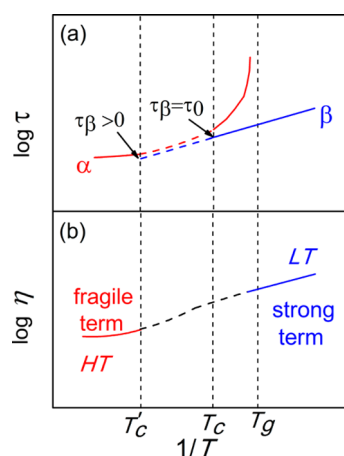dx.doi.org/10.1021/jz500239w | *J. Phys. Chem. Lett.* 2014, 5, 1170−1174

Figure 4. Schematic diagrams of relaxation modes (a) and the F−S transition (b). T_C' is the onset temperature of the F−S transition during cooling, at which the embryonic stage of the slow β relaxation begins. T_C is the critical temperature of the model coupling theory (the merging temperature of the α and slow β relaxations). τ_β at T_C is approximately close to the primitive relaxation time τ_0 of the α relaxation.[27]

that the structural units involved in the slow β relaxation are more comparable (e.g., in cluster size) to those involved in the α relaxation. This is why the smaller r corresponds to a more distinct F−S transition, that is, a larger f.

The negative $f−r$ relationship (in Figure 2) can be explained by the scenario in Figure 3b, that is, the F−S transition in MGFLs is associated with the changes of the mechanism of the slow β relaxation during cooling. Such changes of mechanism of the slow β relaxation with temperature have been observed in $La_{55}Al_{25}Ni_{20}$ MGFLs.[52] According to this scenario, only the α relaxation occurs at HT in Figure 4a. The slow β relaxation begins to occur at T_C' in the embryonic form and also begins to compete with the α relaxation mode. When the liquid enters further deep into the supercooled region, the slow β relaxation diverges from the α relaxation at around T_C ($T_C = 1.2T_g$[53]). Due to the freezing-in of the α relaxation with further cooling, only the slow β relaxation acts at LT. In Figure 4a, T_C' is higher than the critical temperature T_C of the mode coupling theory because the former points to the embryonic stage of the slow β relaxation in the α relaxation. In accordance with this, the F−S transitions in Zr-based MGFLs occur at a temperature higher than T_C ($T_C' = 1.4T_g$) during cooling.[6] For $La_{55}Al_{25}Ni_{20}$ GFLs, T_C' lies above $1.3T_g$.[15] Figure 4b shows that the m' and m values are determined by the HT and LT clusters, respectively.[15] In the supercooled region, the HT and LT clusters compete with each other, leading to the F−S transition. By comparisons between Figure 4a and b, it can be stated that the structure units involved in the α and the slow β relaxations mainly contribute to the fragile term at HT and the strong term at LT, respectively. The characteristics of the F−S transition are then determined by the competition between the α and the slow β relaxations in the supercooled region. This is why the relaxation competition parameter r determines the extent of the F−S transition during cooling in MGFLs.

In summary, we have obtained compelling experimental evidence for the correlation between the F−S transition and the relaxation modes in MGFLs. There is an inverse exponential relationship between the F−S transition extent parameter f and the relaxation competition parameter r. Such a relationship

could explain why the F−S transition cannot be detected in some small molecule organic glass formers and polymers because their r values are so large that their f values tend to 1. Our finding implies that the F−S transition in MGFLs could be closely associated with the splitting of the slow β relaxation from the α relaxation when dropping to a critical temperature, that is, with the discontinuous changes of the slow β relaxation mode. The extent of the F−S transition is mainly determined by the degree of the comparability in structure units between the α and the slow β relaxations. This work helps to uncover the structural origin of the F−S transition in the framework of the relaxation modes in GFLs and also to understand different relaxation modes in the merging region above the T_C of the mode coupling theory.

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Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Ito, K.; Moynihan, C. T.; Angell, C. A. Thermodynamic Determination of Fragility in Liquids and a Fragile-to-Strong Liquid Transition in Water. *Nature* **1999**, *398*, 492−495.

(2) Saika-Voivod, I.; Poole, P. H.; Sciortino, F. Fragile-to-Strong Transition and Polyamorphism in the Energy Landscape of Liquid Silica. *Nature* **2001**, *412*, 514−517.

(3) Swenson, J.; Bergman, R.; Longeville, S. A Neutron Spin−Echo Study of Confined Water. *J. Chem. Phys.* **2001**, *115*, 11299−11305.

(4) Buhot, A.; Garrahan, J. P. Crossover from Fragile to Strong Glassy Behaviour in the Spin Facilitated Chain Model. *J. Phys.: Condens. Matter* **2002**, *14*, 1499.

(5) Faraone, A.; Liu, L.; Mou, C.-Y.; Yen, C.-W.; Chen, S.-H. Fragile-to-Strong Liquid Transition in Deeply Supercooled Confined Water. *J. Chem. Phys.* **2004**, *121*, 10843−10846.

(6) Li, J. J. Z.; Rhim, W. K.; Kim, C. P.; Samwer, K.; Johnson, W. L. Evidence for a Liquid−Liquid Phase Transition in Metallic Fluids Observed by Electrostatic Levitation. *Acta Mater.* **2011**, *59*, 2166−2171.

(7) Evenson, Z.; Schmitt, T.; Nicola, M.; Gallino, I.; Busch, R. High Temperature Melt Viscosity and Fragile to Strong Transition in Zr−Cu−Ni−Al−Nb(Ti) and $Cu_{47}Ti_{34}Zr_{11}Ni_8$ Bulk Metallic Glasses. *Acta Mater.* **2012**, *60*, 4712−4719.

(8) Zhang, C. Z.; Hu, L. N.; Yue, Y. Z.; Mauro, J. C. Fragile-to-Strong Transition in Metallic Glass-Forming Liquids. *J. Chem. Phys.* **2010**, *133*, 014508.

(9) Zhang, C. Z.; Hu, L. N.; Bian, X. F.; Yue, Y. Z. Fragile-to-Strong Transition in Al−Ni−M (M=La, Pr, Nd) Metallic Glasses. *Chin. Phys. Lett.* **2010**, *27*, 116401.

(10) Zhou, C.; Sun, Q. J.; Zhang, C. Z.; Yue, Y. Z.; Hu, L. N. Fragile-to-Strong Transition in CuZr(Al) Metallic Glass-Forming Liquids. In preparation.

(11) Mauro, J. C.; Yue, Y. Z.; Ellison, A. J.; Gupta, P. K.; Allan, D. C. Viscosity of Glass-Forming Liquids. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 19780−19784.

(12) Jagla, E. A. A Model for the Fragile-to-Strong Transition in Water. *J. Phys.: Condens. Matter* **1999**, *11*, 10251.

(13) Tanaka, H. A New Scenario of the Apparent Fragile-to-Strong Transition in Tetrahedral Liquids: Water as an Example. *J. Phys.: Condens. Matter* **2003**, *15*, L703.

(14) Liu, L.; Chen, S.-H.; Faraone, A.; Yen, C.-W.; Mou, C.-Y. Pressure Dependence of Fragile-to-Strong Transition and a Possible Second Critical Point in Supercooled Confined Water. *Phys. Rev. Lett.* **2005**, *95*, 117802.

(15) Hu, L. N.; Zhou, C.; Zhang, C. Z.; Yue, Y. Z. Thermodynamic Anomaly of the Sub-T_g Relaxation in Hyperquenched Metallic Glasses. *J. Chem. Phys.* **2013**, *138*, 174508.

(16) Johari, G. P.; Goldstein, M. Viscous Liquids and the Glass Transition. II. Secondary Relaxations in Glasses of Rigid Molecules. *J. Chem. Phys.* **2003**, *53*, 2372−2388.

(17) Debenedetti, P. G.; Stillinger, F. H. Supercooled Liquids and the Glass Transition. *Nature* **2001**, *410*, 259−267.

(18) Fan, G. J.; Fecht, H. J. A Cluster Model for the Viscous Flow of Glass-Forming Liquids. *J. Chem. Phys.* **2002**, *116*, 5002−5006.

(19) Ngai, K. L. An Extended Coupling Model Description of the Evolution of Dynamics with Time in Supercooled Liquids and Ionic Conductors. *J. Phys.: Condens. Matter* **2003**, *15*, S1107.

(20) Ngai, K. L.; Capaccioli, S. On the Relevance of the Coupling Model to Experiments. *J. Phys.: Condens. Matter* **2007**, *19*, 205114.

(21) Williams, G.; Watts, C. D. In *NMR: Basic Principles and Progress*; Dielh, P., Ed.; Springer-Verlag: Berlin, 1971; p 271.

(22) Williams, G. Molecular Aspects of Multiple Dielectric Relaxation Processes in Solid Polymers. *Adv. Polym. Sci.* **1979**, *33*, 59−92.

(23) Zhao, Z. F.; Wen, P.; Shek, C. H.; Wang, W. H. Measurements of Slow β-Relaxations in Metallic Glasses and Supercooled Liquids. *Phys. Rev. B* **2007**, *75*, 174201.

(24) Yu, H.-B.; Wang, W.-H.; Samwer, K. The β Relaxation in Metallic Glasses: An Overview. *Mater. Today* **2013**, *16*, 183−191.

(25) Hu, L. N.; Yue, Y. Z. Secondary Relaxation Behavior in a Strong Glass. *J. Phys. Chem. B* **2008**, *112*, 9053−9057.

(26) Hu, L. N.; Yue, Y. Z. Secondary Relaxation in Metallic Glass Formers: Its Correlation with the Genuine Johari−Goldstein Relaxation. *J. Phys. Chem. C* **2009**, *113*, 15001−15006.

(27) Tanaka, H. Origin of the Excess Wing and Slow β Relaxation of Glass Formers: A Unified Picture of Local Orientational Fluctuations. *Phys. Rev. E* **2004**, *69*, 021502.

(28) Hedström, J.; Swenson, J.; Bergman, R.; Jansson, H.; Kittaka, S. Does Confined Water Exhibit a Fragile-to-Strong Transition? *Eur. Phys. J.: Spec. Top.* **2007**, *141*, 53−56.

(29) Yu, H. B.; Wang, Z.; Wang, W. H.; Bai, H. Y. Relation between β Relaxation and Fragility in LaCe-Based Metallic Glasses. *J. Non-Cryst. Solids* **2012**, *358*, 869−871.

(30) Wang, W. H. Correlation between Relaxations and Plastic Deformation, and Elastic Model of Flow in Metallic Glasses and Glass-Forming Liquids. *J. Appl. Phys.* **2011**, *110*, 053521.

(31) Ngai, K. L.; Capaccioli, S. Relation between the Activation Energy of the Johari−Goldstein β Relaxation and T_g of Glass Formers. *Phys. Rev. E* **2004**, *69*, 031501.

(32) Meng, Q. G.; Zhang, S. G.; Li, J. G.; Bian, X. F. Strong Liquid Behavior of $Pr_{55}Ni_{25}Al_{20}$ Bulk Metallic Glass. *J. Alloys Compd.* **2007**, *431*, 191−196.

(33) Guo, J.; Bian, X. F.; Zhao, Y.; Zhang, S. J.; Li, T. B.; Wang, C. D. Correlation between the Fragility of Supercooled Liquids and Thermal Expansion in the Glassy State for Gd-Based Glass-Forming Alloys. *J. Phys.: Condens. Matter* **2007**, *19*, 116103.

(34) Guo, J.; Bian, X. F. A Correlation between Superheated Liquid Fragility and Supercooled Liquid Fragility in La- and Sm-Based Glass-Forming Alloys. *J. Alloys Compd.* **2010**, *504*, S205−S207.

(35) Bian, X. F.; Sun, B. A.; Hu, L. N.; Jia, Y. B. Fragility of Superheated Melts and Glass-Forming Ability in Al-Based Alloys. *Phys. Lett. A* **2005**, *335*, 61−67.

(36) Lu, Z. P.; Li, Y.; Liu, C. T. Glass-Forming Tendency of Bulk La−Al−Ni−Cu−(Co) Metallic Glass-Forming Liquids. *J. Appl. Phys.* **2002**, *93*, 286−290.

(37) Yu, H. B.; Wang, W. H.; Bai, H. Y.; Wu, Y.; Chen, M. W. Relating Activation of Shear Transformation Zones to B Relaxations in Metallic Glasses. *Phys. Rev. B* **2010**, *81*, 220201.

(38) Qin, Q.; McKenna, G. B. Correlation between Dynamic Fragility and Glass Transition Temperature for Different Classes of Glass Forming Liquids. *J. Non-Cryst. Solids* **2006**, *352*, 2977−2985.

(39) Hodge, I. M. Strong and Fragile Liquids — A Brief Critique. *J. Non-Cryst. Solids* **1996**, *202*, 164−172.

(40) Komatsu, T. Application of Fragility Concept to Metallic Glass Formers. *J. Non-Cryst. Solids* **1995**, *185*, 199−202.

(41) Qiao, J. C.; Pelletier, J. M.; Wang, Q.; Jiao, W.; Wang, W. H. On Calorimetric Study of the Fragility in Bulk Metallic Glasses with Low Glass Transition Temperature: $(Ce_{0.72}Cu_{0.28})_{90−x} Al_{10}Fe_x$ (x = 0, 5 or 10) and $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$. *Intermetallics* **2011**, *19*, 1367−1373.

(42) Zhao, Z. F.; Wen, P.; Shek, C. H.; Wang, W. H. Relaxation Behavior on High Frequency Profile in Strong/Fragile Metallic Glass-Forming Systems. *J. Non-Cryst. Solids* **2010**, *356*, 1198−1200.

(43) Ngai, K. L. Relation between Some Secondary Relaxations and the α Relaxations in Glass-Forming Materials According to the Coupling Model. *J. Chem. Phys.* **1998**, *109*, 6982−6994.

(44) Döß, A.; Paluch, M.; Sillescu, H.; Hinze, G. Dynamics in Supercooled Polyalcohols: Primary and Secondary Relaxation. *J. Chem. Phys.* **2002**, *117*, 6582−6589.

(45) Mauro, J. C.; Loucks, R. J. Impact of Fragility on Enthalpy Relaxation in Glass. *Phys. Rev. E* **2008**, *78*, 021502.

(46) Mauro, J. C.; Allan, D. C.; Potuzak, M. Nonequilibrium Viscosity of Glass. *Phys. Rev. B* **2009**, *80*, 094204.

(47) Mauro, J. C. Effect of Fragility on Relaxation of Density Fluctuations in Glass. *J. Non-Cryst. Solids* **2011**, *357*, 3520−3523.

(48) Cao, W. Q.; Shang, X. Z. Viscosity−Temperature Relation of Aggregation Energies in Glass Forming Process. *Phys. Procedia* **2013**, *48*, 120−124.

(49) Mallamace, F.; Branca, C.; Corsaro, C.; Leone, N.; Spooren, J.; Chen, S.-H.; Stanley, H. E. Transport Properties of Glass-Forming Liquids Suggest That Dynamic Crossover Temperature Is As Important As the Glass Transition Temperature. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 22457−22462.

(50) Wang, L.-M.; Mauro, J. C. An Upper Limit to Kinetic Fragility in Glass-Forming Liquids. *J. Chem. Phys.* **2011**, *134*, 044522.

(51) Garwe, F.; Schönhals, A.; Lockwenz, H.; Beiner, M.; Schröter, K.; Donth, E. Influence of Cooperative A Dynamics on Local β Relaxation during the Development of the Dynamic Glass Transition in Poly(*n*-alkyl methacrylate)s. *Macromolecules* **1996**, *29*, 247−253.

(52) Hu, L. N.; Zhang, C. Z.; Yue, Y. Z. Structural Evolution during the Sub-T_g Relaxation of Hyperquenched Metallic Glasses. *Appl. Phys. Lett.* **2010**, *96*, 221908.

(53) Hu, L. N.; Zhang, C. Z.; Yue, Y. Z.; Bian, X. F. A New Threshold of Uncovering the Nature of Glass Transition: The Slow β Relaxation in Glassy States. *Chin. Sci. Bull.* **2010**, *55*, 457−472.

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