

Intrinsic correlation between fragility and bulk modulus in metallic glasses

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A systematic study on the available data of 26 metallic glasses shows that there is an intrinsic correlation between fragility of a liquid and bulk modulus of its glass. The underlying physics can be rationalized within the formalism of potential energy landscape thermodynamics. It is surprising to find that the linear correlation between the fragility and the bulk-shear modulus ratio exists strictly at either *absolute zero temperature* or *very high frequency*. Further analyses indicate that a real flow event in bulk metallic glasses is *shear dominant*, and fragility is in *inverse* proportion to shear-induced bulk dilatation. Finally, extension of these findings to *nonmetallic* glasses is discussed.

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I. INTRODUCTION

Understanding of the material-dependent slowing down dynamics is one of the central subjects in glass physics. In terms of the concept of fragility introduced by Angell,¹ the glass-forming systems can be classified into “strong” or “fragile” pattern. The kinetic fragility m is defined as

$$m = \left. \frac{\partial \log(\eta/\eta_\infty)}{\partial(T_g/T)} \right|_{T=T_g}, \quad (1)$$

where η_∞ is the limiting high-temperature shear viscosity and T_g is the glass transition temperature. Here, the dimensionless fragility index, a measure of deviation from the Arrhenius behavior in the temperature-dependent viscosity, opens a new window into the understanding of glass transition and its slowing down dynamics. The kinetic fragility was found to be correlated with other properties characterizing the liquid side of glass transition² and low-temperature properties of glasses such as vibration.^{3,4} An unexpected linear correlation between bulk-shear modulus ratio (K_∞/G_∞) and fragility in nonmetallic glass was reported by Novikov and Sokolov.⁵ Due to the technological and the scientific significance of this surprising finding, it has attracted a lot of discussions.^{6–10} However, the question whether such a linear correlation universally exists still remains open up to now. As for metallic glasses, a number of important correlations among their properties have been revealed.^{11–16} Recently, Novikov and Sokolov¹⁷ discovered that there is also a linear correlation between the bulk-shear modulus ratio and fragility in metallic glasses, and the deviation from the linear correlation is due to the material-specific free electron gas. In this paper, a systematic study on the correlation between fragility and elastic modulus in metallic glasses is done, and further, its underlying physics is discussed.

II. EXPERIMENTAL OBSERVATIONS

Table I lists the measured physical properties of 26 metallic glasses,¹⁸ such as density ρ , molar mass M , bulk modulus K , shear modulus G , glass transition temperature T_g , and fragility m . It is well known that values of m can be directly

taken by using the Vogel-Fulcher-Tamman (VFT) equation fits to viscosity or relaxation time data.¹ This is the kinetic method. On the other hand, the liquid fragility can be determined from a purely thermodynamic way, i.e., the heating rate dependent T_g .^{15,20} Let us note that the fragility values of metallic glasses numbered as 1–8, 14, 15, 17, and 18 in Table I are given by the thermodynamic method, whereas the others are obtained from viscosity or relaxation data. Besides, we also note that the fragility values are mostly derived from the latest literature such as Refs. 9, 15, and 17. Previous studies have demonstrated that the heating rate dependent T_g describes the fragility equally well as complementary viscosity or relaxation time measurements.^{29–31} Thus, the following results according to these values in Table I are believable, and the unavoidable slight error due to different measurements cannot significantly change the intrinsic relationship among the parameters listed in Table I. As shown in Fig. 1, there seems no clear linear relation between fragility and K [or G , K/G , and the Poisson ratio, $\nu=1/2-3/(6K/G+2)$] just as Battazzati⁷ and Johari⁹ observed. However, the scrupulous examination shows that a parameter combination, $mRT_g/(M/\rho)$, exhibits a striking linear correlation with K (see Fig. 2) regardless of chemical components, structural details, etc., and the best fit of data is given by

$$mRT_g/(M/\rho) - 0.729 = 0.198K, \quad (2)$$

where M/ρ is the molar volume V_m . That is, the correlation between m and K does not follow a simple linear relation, and the influence of material parameters such as T_g , M , and ρ should be involved.

III. THEORY

Potential energy landscape (PEL) is an ideal method to describe the behavior of disordered systems,^{32,33} which can be used to reveal the underlying physics of the linear correlation in Eq. (2). For simplicity, let us assume that the potential energy of a system with N pointlike constituent particles only depends on the spatial location \mathbf{r}_i for each particle in a $(3N+1)$ -dimensional hypersurface. Intuitively, the state of

TABLE I. Physical properties of 26 metallic glasses, such as density ρ , molar mass M , bulk modulus K , shear modulus G , glass transition temperature T_g , and fragility m .

	Metallc glasses	ρ (g/cm ³)	M (g/mol)	K (GPa)	G (GPa)	T_g (K)	m	Refs.
1	Ce ₇₀ Al ₁₀ Ni ₁₀ Cu ₁₀	6.67	113	27	11.5	359	21	7, 12, and 13
2	Cu ₄₆ Zr ₄₆ Al ₈	7.23 ^a	73.3	116.4	34.3	701	43	15
3	Cu ₄₆ Zr ₄₆ Al ₇ Gd ₁	7.40	74.6	123.7	32.9	720	29	15
4	Fe ₇₀ P ₁₀ C ₅ B ₅ Si ₃ Al ₅ Ga ₂	6.24 ^b	46.9	113.4	58.5	736 ^c	34	15
5	Ho ₃₉ Al ₂₅ Co ₂₀ Y ₁₆	6.50 ^b	97.1	63.60	26.2	630	49	15
6	La ₅₅ Al ₂₅ Cu ₁₀ Ni ₅ Co ₅	6.00	95.4	44.2	15.6	430	28	13, 15, and 19
7	Nd ₆₀ Fe ₂₀ Co ₁₀ Al ₁₀	7.00	106	46.54	19.44	493	33	15, 17, and 19
8	Pd _{39.1} Ni _{10.1} Cu _{29.9} P _{20.9}	9.2	73.0	158.7	35.2	576	52	15
9	Pd ₃₉ Ni ₁₀ Cu ₃₀ P ₂₁	9.152	72.9	159.1	35.1	586	55	15 and 17
10	Pd ₄₀ Ni ₁₀ Cu ₃₀ P ₂₀	9.3	73.7	146	33	560	52	13, 20, and 21
11	Pd ₄₀ Ni ₄₀ P ₂₀	9.405	72.2	185	38.6	602	54	15, 19, and 22
12	Pd ₄₈ Ni ₃₂ P ₂₀	9.83	76	176.7	36.2	590	48	15 and 17
13	Pd ₆₄ Ni ₁₆ P ₂₀	10.1	83.7	166	32.7	582	51	13, 21, and 23
14	Pd _{77.5} Cu ₆ Si _{16.5}	10.4	90.9	167	31.5	635	52	7, 23, and 24
15	Pr ₆₀ Al ₁₀ Ni ₁₀ Cu ₂₀	6.90	106	45.2	13.6	409	31	20 and 25
16	Pt ₆₀ Ni ₁₅ P ₂₅	15.7	133	202	33.8	500	86	13 and 26
17	Mg ₆₅ Cu ₂₅ Y ₁₀	3.978	40.6	44.71 ^d	19.6 ^d	402	41	7, 21, and 23
18	Mg ₆₅ Cu ₂₅ Gd ₁₀	4.04	47.4	46.3	18.6	417	41	13 and 15
19	Mg ₆₅ Cu ₂₅ Tb ₁₀	3.98	47.4	44.7	19.6	414	47	15 and 17
20	Ni ₆₀ Nb ₃₅ Sn ₅	8.64	74.3	267	66.32	885	70	15 and 17
21	Ni ₆₄ Pd ₁₆ P ₂₀	8.75	61.3	169.8	37.9	587	50	15 and 17
22	Zr ₄₁ Ti ₁₄ Cu _{12.5} Ni ₁₀ Be _{22.5}	6.12	59.9	114.7	37.4	627	50	7, 17, and 21
23	Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni ₁₀ Be _{22.5}	5.9	60.0	114.1	34.1	618	50	13 and 27
24	Zr _{46.75} Ti _{8.25} Cu _{7.5} Ni ₁₀ Be _{27.5}	6.01	59.5	113.38	35.2	590	44	15, 19, and 27
25	Zr ₅₅ Al ₁₉ Co ₁₉ Cu ₇	6.2	101.7	114.9	37.6	733	72 ^e	15 and 17
26	Zr ₆₅ Al ₁₀ Ni ₁₀ Cu ₁₅	6.75 ^f	77.4	106.65	30.27	653	30	15, 19, and 28

^aValue for Cu₄₆Zr₄₂Al₇Y₅.^bCalculated by atom mole ratio.^cValue for Fe₈₀P₁₃C₇.^dValues for Mg₆₅Cu₂₅Tb₁₀.^eValue for Zr₅₅Al_{22.5}Co_{22.5}.^fValue for Zr₆₅Cu_{17.5}Al_{7.5}Ni₁₀.

such a system can be represented by a point s on or above the hypersurface. By analogy to Earth's topographic maps, Stillinger and Weber provided a formally exact partitioning of the configurational space as a sum of distinct basins, associating with each local minimum of the potential energy surface, namely, an inherent structure (IS). The purpose is to assign any configuration of atoms uniquely to one local minimum by the steepest descent path; if it is not at a minimum, the displacement exhibited by the system is simply regarded as a "vibrational," possibly anharmonic in character, displacement. Thus, packing and vibration effects can be cleanly separated.

The system free energy in an IS can be expressed as a sum of a configurational contribution, accounting for the number of the available basins, and a vibrational one, expressing the free energy of the system when constrained in one of the basins.^{34,35} Here, the Helmholtz free energy $F(T, V)$ of a metallic glass (unit mass) at the temperature below T_g can also be written as

$$F(T, V) = F_{conf}(T, V) + F_{vib}(T, V), \quad (3)$$

where the first term on the right hand side is the configurational portion denoted as $F_{conf} = U(V) - TS_{conf}$, with $U(V)$ the average specific potential energy of internal energy and $-TS_{conf}$ the configurational contribution to F_{conf} that switches off due to $T < T_g$. The second term, $F_{vib} = U_{vib} - TS_{vib}$, indicates the vibrational part, where S_{vib} is the vibrational entropy due to departure from the local minimum and the kinetic part of internal energy U_{vib} can be negligible. Since a metallic glass is an isotropic body, its potential energy can be assumed as³⁶

$$U(V) = -A/V^{\alpha/3} + B/V^{\beta/3} \quad (\alpha > \beta), \quad (4)$$

where A and B are constants. Here, the first term represents the energy of the attractive interaction and the second term is the energy of repulsion. The values of α and β are determined by material composition and structure. A glass at tem-

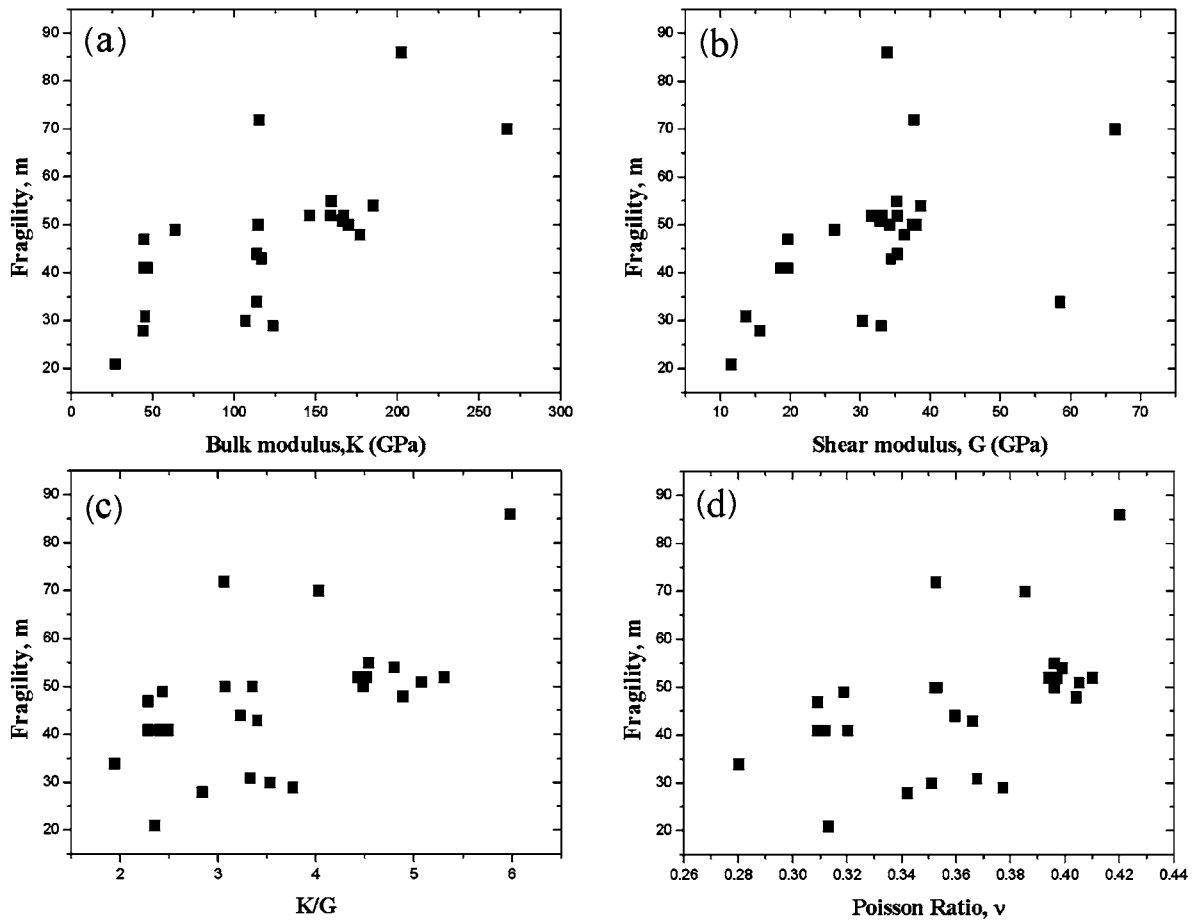


FIG. 1. Fragility versus (a) bulk modulus K , (b) shear modulus G , (c) bulk-shear modulus ratio, K/G , and (d) Poisson ratio ν .

perature below T_g is at or near a potential energy minimum or an IS. Its potential energy is $U_0=U(V_0)$ due to $(\partial U/\partial V)_{V_0}=0$. According to the thermodynamics,³⁷ the isothermal bulk modulus at $T < T_g$ can be obtained by

$$K = -\alpha\beta\rho U_0/9 - (T/\rho)(\partial^2 S_{vib}/\partial V^2)_{T,V_0}. \quad (5)$$

Note that Eqs. (3) and (4) are used in deriving this equation. Many studies³⁸ have demonstrated that the viscosity-temperature relation of supercooled liquids for metallic glass formers, especially approaching T_g , can be described well by the VFT equation.³⁹ In terms of U_0 , the VFT equation can be expressed as^{40,41}

$$\eta = \eta_\infty \exp\{-lMU_0/[R(T-T_0)]\}, \quad (6)$$

where l is a numerical factor, R is a gas constant, and T_0 is the Vogel temperature. Compared to the usual expression of the VFT equation, $\eta = \eta_\infty \exp[B/(T-T_0)]$, where B is the activation energy of viscous flow, we find $B = -lMU_0/R$. So, Eq. (6) implies that the activation energy of viscous flow when $T > T_0$ is proportional to the IS potential energy U_0 . Based on this assumption, Gemant⁴¹ established a relation between bulk modulus and viscosity of plastics. Applying the obtained relation to glass materials exhibits a good correlation between room-temperature elastic modulus and viscosity at high temperature.⁴¹ Also, the assumption is consistent with the basic tenet of PEL, namely, “the existence of potential energy barriers large compared to thermal energy are intrinsic to the occurrence of the glassy state, and dominate flow, at least at low temperature.”³² Inserting Eq. (6) into Eq.

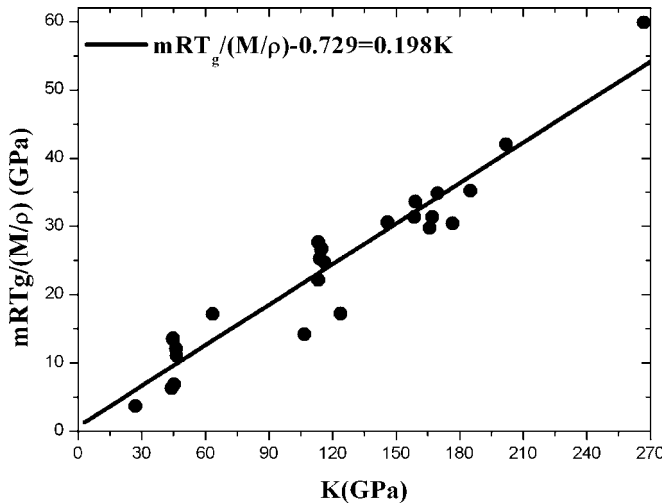


FIG. 2. Correlation between $mRT_g/(M/\rho)$ and bulk modulus K in the glassy state, where the straight line is the best fitting results by Eq. (2).

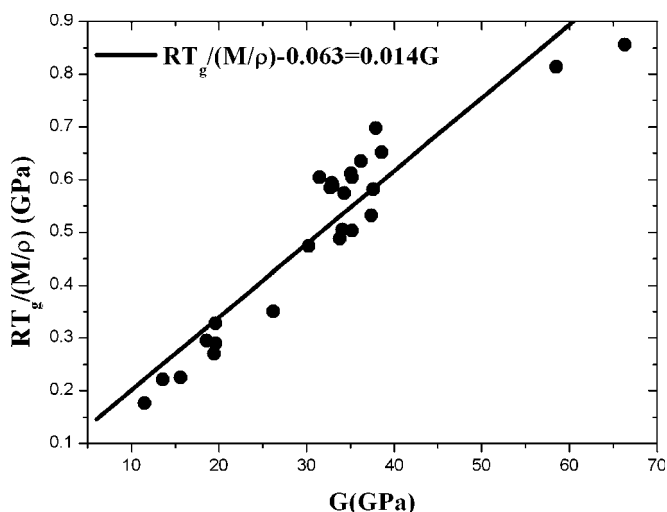


FIG. 3. Correlation between $RT_g/(M/\rho)$ and shear modulus G in the glassy state, where the straight line is the best fitting results by Eq. (8).

(1) yields $U_0 = -mR(T_g - T_0)^2 \ln 10 / (LMT_g)$. Further, according to Eq. (5) and $T_g = T_0[1 + B/(17T_0 \ln 10)]$,¹ we have the following correlation between fragility and bulk modulus:

$$mRT_g/(M/\rho) + L(T) = CK, \quad (7)$$

where $L(T) = C[-(T/\rho)(\partial^2 S_{\text{vib}}/\partial V^2)]_{T,V_0}$ and $C = 9/[1 + 17(T_0/B) \ln 10]/(\alpha\beta \ln 10)$. Surprisingly, Eq. (7) is totally identical to the empirical fitting, i.e., Eq. (2), so long as $L(T) = -0.729$ GPa and $C = 0.198$. It is important to point out that Eq. (7) is valid if temperature is below T_g , and Eq. (6) is only valid when $T > T_0$. The term $L(T)$ reflects the temperature softening effect on bulk modulus, and C is weakly material dependent for metallic glasses according to the fit to experimental data.

IV. DISCUSSION

A. Fragility and bulk-shear modulus ratio

To shed an insight into whether fragility m is correlated linearly with K/G , we examined the data in Table I. A striking linear correlation between $RT_g/(M/\rho)$ and shear modulus G is observed, as shown in Fig. 3. This linear correlation can be best fitted by

$$RT_g/(M/\rho) + H(T) = DG, \quad (8)$$

where $H(T) = -0.063$ GPa, which is temperature dependent like the term $L(T)$ in Eq. (7), and $D = 0.014$. It is worth noting that this intrinsic relation for metallic glasses is consistent with those obtained by Johnson and Somwer¹³ and Yang *et al.*¹⁶ Now, we realize that although the correlation between fragility m and bulk modulus K is characterized explicitly by Eq. (7), the correlation between fragility m and shear modulus G is characterized implicitly by this equation through the parameter $RT_g/(M/\rho)$ that is scaled linearly with G , as shown in Fig. 3. Combining Eq. (7) with Eq. (8), we have the following correlation:

$$m = a(K/G) + b(T; m, G), \quad (9)$$

where $a = C/D$ is a material-independent constant and $b(T; m, G) = [mH(T) - L(T)]/(DG)$ indicates the effect of temperature on modulus. It is easy to see that the linear correlation between m and K/G in Eq. (9) exists only when $b(T; m, G)$ is a material-independent constant. However, this condition is too harsh given that both m and G are highly material dependent. Obviously, m must be strictly proportional to K/G for solid glasses at *absolute zero temperature* or *very high frequency*. Each of these two conditions leads to $L(T) = 0$ and $H(T) = 0$. In fact, the former condition, i.e., the observed correlation at absolute zero temperature, is consistent with the finding of Scopigno *et al.*³ (*vide post*), while the latter implies that fragility is linearly linked to the *instantaneous* bulk-shear modulus ratio.⁵ Both the conditions require that measurements of the elastic constants of glasses be made either at a temperature low enough that molecular motion in structure is kinetically frozen or at a frequency used for ultrasonic measurements high enough that the temperature-dependent fast β relaxational contributions (not only the structure relaxation⁵) are negligible. However, it is almost impossible that the above conditions are strictly satisfied, because, in a real experiment, sound velocity measurements on modulus in the frequency range of 20–50 Hz may not yield elastic properties attributable to vibrations alone, while measurements on solid glasses are usually performed at room temperature. This is why the experimental data do not obey the linear correlation.^{7,9} Our finding that fragility is linearly related to the zero temperature or much higher frequency bulk-shear modulus ratio implies that liquid viscosity is determined by its zero temperature or short-time-scale elastic properties. This seems to be at odds with the prevailing paradigm of glass science,¹⁰ which is embodied in the Adam-Gibbs model.⁴² Nevertheless, according to elastic models of glass forming, the barrier transition for a “flow event” (an atomic rearrangement) does take place on a very short time scale.⁴³ Furthermore, both Egami’s atomistic theory⁸ and the microstructural model of Ichitsubo *et al.*⁶ can perfectly explain the Novikov-Sokolov observations. Actually, in their models, the temperature-dependent modulus was neglected, which corresponds to $b(T; m, G) \equiv 0$ in our case.

B. Shear-induced dilatation

Next, let us discuss the physical pictures behind Eqs. (7) and (8). In soil mechanics, it has been known for years that shear of randomly close-packed grains causes dilatation. The same phenomenon can be applied at the atomic scale. Crystals can deform at constant volume because the periodicity along slip planes provides identical atomic positions for sheared materials. A sheared portion of an amorphous material, on the other hand, does not find such a perfect fit and thus will leave some holes.⁴⁴ It has been recognized that macroscopic flow of an amorphous material occurs as a result of a number of individual atomic jumps or flow events. Thus, a real flow event in bulk metallic glasses must result in shear deformation and an accompanying bulk deformation

(or dilatation). Actually, according to Dyre's shoving model, spherical symmetry in real flow events is probably violated, leading to some compression of surroundings and a contribution to activation energy that is proportional to bulk modulus.⁴⁵ The equivalent PEL of the shoving model also confirmed this point; thereby, activation energy must involve both shear and bulk moduli.⁴⁶ However, which of them controls the activation energy? The elastic models such as rate theory, shoving model, etc., give a theoretical answer and clarify that activation energy is proportional to shear modulus that is a controlling parameter in a real flow event.⁴³ It is of interest to note that our results are consistent with the elastic models from the viewpoint of experimental data for bulk metallic glasses (BMGs). Equation (8) characterizes shear deformation in real flow events, while Eq. (7) determines shear-induced bulk deformation. Based on the physical analogy between the shear transformation zone deformation and glass transition, Yang *et al.* found that the shear yield strength of BMGs at ambient temperature T_0 can be predicted well by a unified parameter, $R(T_g - T_0)/V_m$.¹⁶ Compared to Eq. (8), we find that a compound parameter, RT_g/V_m , can be regarded as a scale on shear yield strength at zero temperature, although $H(T)$ is weakly dependent on T_0 . Data fitting shows that D is a material-independent constant with magnitude of 10^{-2} , which is consistent with the average shear yield strain γ_C observed by Johnson and Samwer.¹³ Thus, D can be considered as an apparent shear yield strain $\hat{\gamma}_C$. The linear correlation between RT_g/V_m and G implies that G is a controlling quantity in real flow events. In parallel with this consideration, it is natural to investigate the relationship between RT_g/V_m and K . Although mRT_g/V_m is proportional to K , RT_g/V_m does not scale with K , i.e., $(RT_g/V_m)/K \sim \hat{\xi}_C \neq \text{const}$, where $\hat{\xi}_C = C/m$ is shear-induced dilatation (with the order of magnitude of 10^{-3}) while shear yielding occurs. It is noted that $\hat{\xi}_C$ is associated with m , and thus highly material specific. Since C is a material-independent constant for metallic glasses, it is easily seen that fragility m is in inverse proportional to $\hat{\xi}_C$. This means that, subjected to same hydrostatic compression, strong glasses are of higher bulk dilatation, while fragile ones have smaller bulk deformation.⁴⁷ The explicit correlation between bulk (not shear) modulus and fragility may result from this highly material-dependent bulk deformation in BMGs.¹⁷

Using a model developed by Knuyt *et al.* based on a Gaussian distribution for the nearest-neighbor distance in an ideal unicomponent metallic glass,⁴⁸ we can approximately calculate the ratio of bulk to shear elastic energy in a flow event with the following equation:

$$\frac{E_{\text{elastic,bulk}}}{E_{\text{elastic,shear}}} = \frac{(1/2)\hat{\xi}_C^2 K}{(3/2)\hat{\gamma}_C^2 G}. \quad (10)$$

Note that this ratio increases with decreasing m and increasing K/G . However, there is a tendency for fragility m to increase with increasing K/G , and vice versa. For BMGs (see Table I), m mostly ranges from 30 to 80, and K/G is in the range 2–5; thus, the range of this ratio of bulk to shear elastic energy in a flow event is usually less than about 10%.

Our result is consistent with the result of 8% calculated by Dyre and Olsen based on PEL⁴⁶ or the 10% calculated recently by Dyre on a standard dipole expansion.⁴⁹ It indicates that the bulk modulus' contribution to the activation energy is much less than that due to shear deformation in a real flow event. Consequently, shear (not bulk) modulus controls the activation energy (that is *shear dominant*) in a real flow event.

C. Comparison with related works

At this point, we briefly discuss related works. Based on local topological instability analysis and the assumption that bulk modulus is almost independent of temperature, Egami¹⁴ predicts that there is a correlation between T_g and bulk modulus K for metallic glasses, $T_g = 6.14 \times 10^{-3} K \langle \Omega \rangle / k_B$. Actually, this assumption is equivalent to the case that the temperature-dependent term $L(T) \rightarrow 0$ in Eq. (7). Thus, Eq. (7) can be converted into

$$T_g = (C/m)(K \langle \Omega \rangle / k_B), \quad (11)$$

where $\langle \Omega \rangle = M / (N_0 \rho)$ is the average atomic volume of a metallic glass with N_0 the Avogadro constant. It is interesting to find that if the fragility value in Eq. (11) is equal to 32.25 (the fragility value of metallic glasses ranges from 21 to 86 in this study), Egami's prediction is recovered.

Also, Eq. (7) leads us directly to an explanation of the striking finding of Scopigno *et al.*³ They found that fragility is proportional to a dimensionless quantity α , i.e., the temperature steepness of the nonergodicity factor at $T \rightarrow 0$.¹² The low-temperature α only depends on the interaction potential and disordered structure. In the harmonic approximation for vibrational dynamics, α can be expressed as³ $\alpha = (MN \sum_p \omega_p^{-2}) / (k_B T_g Q^2)$, where M is the molecular mass, k_B is the Boltzmann constant, N is the number of particles, Q is the wave vector, and p is summed over $3N$ normal modes. In a system consisting of N_0 (the Avogadro constant), α can be converted into $\alpha = (M/\rho) \{ \rho / [Q^2 (1/N_0) \sum_p \omega_p^{-2}] \} / (RT_g)$, where $Q^2 (1/N_0) \sum_p \omega_p^{-2} \propto v_l^{-2}$ with v_l the longitudinal sound velocity.⁵⁰ Because $K \propto \rho v_l^2$, where v_l is proportional to the transverse sound velocity v_t ,³ α reduces to

$$\alpha \propto (M/\rho) K / (RT_g) |_{T \rightarrow 0}. \quad (12)$$

At $T \rightarrow 0$, Eq. (8) becomes $RT_g / (M/\rho) \propto G$. Substituting it into Eq. (12) gives $\alpha \propto (K/G)_{T=0}$. Due to $m \propto (K/G)_{T=0}$, as discussed above, the finding of Scopigno *et al.*, i.e., $m \propto \alpha$, is also recovered. It is easy to see that the low-temperature α can also be determined by elastic modulus at zero temperature. However, modulus measurements on metallic glasses are usually performed at room temperature. So, it is impossible to calculate the low-temperature α by using the data listed in Table I, whereas Scopigno *et al.*³ cleverly derived the parameter α from the IXS data available for glasses at low temperature.

Finally, to survey the universality of two correlations in Eqs. (7) and (8), let us consider 11 nonmetallic glasses, including BeF₂, B₂O₃, SiO₂, GeO₂, AS₂S₃, CKN, glycerol, salol, *m*-toluidine, OTP, and *m*-TCP.^{3,5} As shown in Fig. 4,

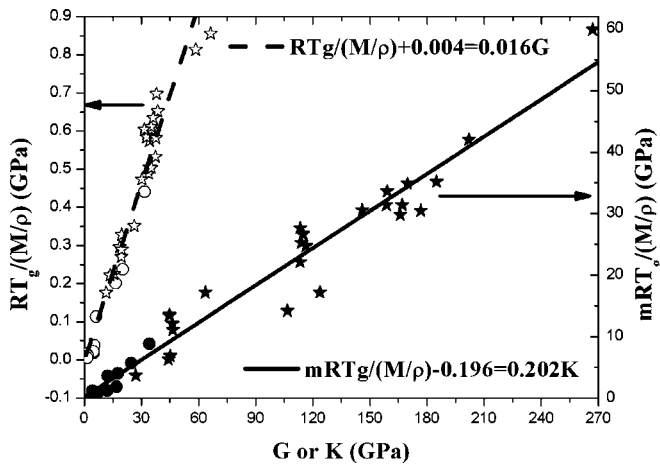


FIG. 4. $mRT_g/(M/\rho)$ versus K and $RT_g/(M/\rho)$ versus G for metallic and nonmetallic glasses. Black and open stars: metallic glasses; black and open circles: nonmetallic glasses.

the linear relationship indicates that the observed intrinsic correlations might be more general although the fitting parameters are not constants. Unfortunately, there are not enough glass formers whose relevant data are all known.

Thus, further work is needed to check the universality of these intrinsic correlations.

V. CONCLUSIONS

In conclusion, an intrinsic correlation between fragility and bulk modulus for 26 metallic glasses was revealed, which could be rationalized in terms of PEL thermodynamics. We found that fragility (the degree of non-Arrhenius viscosity of liquids) can be determined by zero-temperature or short-time-scale mechanical properties of solid glasses. Moreover, an inverse linear correlation between fragility and bulk dilatation induced by shear-dominant activation energy was discovered. These observed intrinsic correlations may be extended to *nonmetallic* glasses. We believe that these findings are of importance for understanding relationships between microstructure and mechanical properties in BMGs.

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- ¹C. A. Angell, *J. Non-Cryst. Solids* **73**, 1 (1985); **131-133**, 13 (1991); R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, *J. Chem. Phys.* **99**, 4201 (1993); C. A. Angell, *Science* **267**, 1924 (1995).
- ²A. P. Sokolov, E. Rössler, A. Kisliuk, and D. Quitmann, *Phys. Rev. Lett.* **71**, 2062 (1993); K. Ngai and O. Yamamuro, *J. Chem. Phys.* **23**, 10403 (1999); L.-M. Martinez and C. A. Angell, *Nature (London)* **410**, 663 (2001); S. Venkataraman, K. Biswas, B. C. Wei, D. J. Sordelet, and J. Eckert, *J. Phys. D* **39**, 2600 (2006).
- ³T. Scopigno, G. Ruocco, F. Sette, and G. Monaco, *Science* **302**, 849 (2003); U. Buchenau and A. Wischnewski, *Phys. Rev. B* **70**, 092201 (2004).
- ⁴Yong Li, H. Y. Bai, W. H. Wang, and K. Samwer, *Phys. Rev. B* **74**, 052201 (2006).
- ⁵V. N. Novikov and A. P. Sokolov, *Nature (London)* **431**, 961 (2004).
- ⁶T. Ichitsubo, E. Matsubara, T. Yamamoto, H. S. Chen, N. Nishiyama, J. Saida, and K. Anazawa, *Phys. Rev. Lett.* **95**, 245501 (2005).
- ⁷L. Battazzati, *Mater. Trans.* **46**, 2915 (2005).
- ⁸T. Egami, *Intermetallics* **14**, 882 (2006).
- ⁹G. P. Johari, *Philos. Mag.* **86**, 1567 (2006); Spyros N. Yannopoulos and G. P. Johari, *Nature (London)* **442**, E7 (2006).
- ¹⁰J. C. Dyre, *Nat. Mater.* **3**, 749 (2004).
- ¹¹A. L. Greer, *Science* **267**, 1947 (1995); M. F. Ashby and A. L. Greer, *Scr. Mater.* **54**, 321 (2005).
- ¹²J. J. Lewandowski, W. H. Wang, and A. L. Greer, *Philos. Mag. Lett.* **85**, 77 (2005).

- ¹³W. L. Johnson and K. Samwer, *Phys. Rev. Lett.* **95**, 195501 (2005).
- ¹⁴T. Egami, *Rep. Prog. Phys.* **47**, 1601 (1984); *Mater. Sci. Eng., A* **226-228**, 261 (1997); S. P. Chen, T. Egami, and V. Vitek, *Phys. Rev. B* **37**, 2440 (1988).
- ¹⁵W. H. Wang, *J. Non-Cryst. Solids* **351**, 1481 (2005); *J. Appl. Phys.* **99**, 1 (2006).
- ¹⁶B. Yang, C. T. Liu, and T. G. Nieh, *Appl. Phys. Lett.* **88**, 221911 (2006).
- ¹⁷V. N. Novikov and A. P. Sokolov, *Phys. Rev. B* **74**, 064203 (2006).
- ¹⁸At present, only 26 metallic glasses, whose relevant data are all known, can be found from the literature.
- ¹⁹Y. Kawamura, T. Nakamura, H. Kato, H. Mano, and A. Inoue, *Mater. Sci. Eng., A* **304-306**, 674 (2001).
- ²⁰Z. F. Zhao, Z. Zhang, P. Wen, M. X. Pan, D. Q. Zhao, W. H. Wang, and W. L. Wang, *Appl. Phys. Lett.* **82**, 4699 (1983).
- ²¹L. N. Hu, X. F. Bian, W. M. Wang, G. R. Liu, and Y. B. Jia, *J. Phys. Chem. B* **109**, 13737 (2005).
- ²²E. F. Lambson, W. A. Lambson, J. E. Macdonald, M. R. J. Gibbs, G. A. Saunders, and D. Turnbull, *Phys. Rev. B* **33**, 2380 (1986).
- ²³D. N. Perera, *J. Phys.: Condens. Matter* **11**, 3807 (1999).
- ²⁴H. S. Chen, *Scr. Metall.* **9**, 411 (1975).
- ²⁵S. Li *et al.*, *Sci. Technol. Adv. Mater.* **6**, 823 (2005).
- ²⁶T. Komatsu, *J. Non-Cryst. Solids* **185**, 199 (1995).
- ²⁷Y. Zhao, X. F. Bian, K. B. Yin, J. K. Zhou, J. Y. Zhang, and X. X. Hou, *Physica B* **349**, 327 (2004).
- ²⁸Y. X. Wei, B. Zhang, R. J. Wang, M. X. Pan, D. Q. Zhao, and W. H. Wang, *Scr. Mater.* **54**, 599 (2006).
- ²⁹R. Busch, E. Bakke, and W. L. Johnson, *Acta Mater.* **46**, 475

- (1998).
- ³⁰K. Ito, C. T. Moynihan, and C. A. Angell, *Nature (London)* **398**, 492 (1999).
- ³¹B. Zhang, R. J. Wang, D. Q. Zhao, M. X. Pan, and W. H. Wang, *Phys. Rev. B* **70**, 224208 (2004).
- ³²M. Goldstein, *J. Chem. Phys.* **51**, 3728 (1969); F. H. Stillinger and T. A. Weber, *Science* **255**, 983 (1984); F. H. Stillinger, *ibid.* **267**, 1935 (1995); F. Sciortino, W. Kob, and P. Tartaglia, *Phys. Rev. Lett.* **83**, 3214 (1999); P. G. Debenedetti and F. H. Stillinger, *Nature (London)* **410**, 259 (2001).
- ³³C. A. Angell, *Nature (London)* **393**, 521 (1998).
- ³⁴S. Sastry, *Nature (London)* **409**, 164 (2001).
- ³⁵E. LaNave, S. Mossa, and F. Sciortino, *Phys. Rev. Lett.* **88**, 225701 (2002).
- ³⁶R. H. Fowler, *Statistical Mechanics* (Macmillan, New York, 1936).
- ³⁷Callen and B. Herbert, *Thermodynamics* (Wiley, New York, 1960).
- ³⁸C. A. Volkert and F. Spaepen, *Mater. Sci. Eng.* **97**, 449 (1988); W. L. Johnson, *Mater. Res. Bull.* **24**, 42 (1999).
- ³⁹H. Vogel, *Phys. Z.* **22**, 645 (1921); G. S. Fulcher, *J. Am. Ceram. Soc.* **8**, 339 (1925); G. Tamman and W. Hesse, *Z. Anorg. Allg. Chem.* **156**, 245 (1926).
- ⁴⁰J. M. Burgers, *Second Report on Viscosity and Plasticity* (Normann, New York, 1938), Chap. I.
- ⁴¹A. Gemant, *J. Appl. Phys.* **12**, 680 (1941).
- ⁴²G. Adam and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).
- ⁴³J. C. Dyre, *Rev. Mod. Phys.* **78**, 953 (2006).
- ⁴⁴F. Spaepen, *Nat. Mater.* **5**, 7 (2006); J. Li, F. Spaepen, and T. C. Hufnagel, *Philos. Mag. A* **82**, 2623 (2002).
- ⁴⁵J. C. Dyre, *J. Non-Cryst. Solids* **235-237**, 142 (1998); J. C. Dyre, N. B. Olsen, and T. Christensen, *Phys. Rev. B* **53**, 2171 (1996).
- ⁴⁶J. C. Dyre and N. B. Olsen, *Phys. Rev. E* **69**, 042501 (2004).
- ⁴⁷W. H. Wang, P. Wen, L. M. Wang, Y. Zhang, M. X. Pan, D. Q. Zhao, and R. J. Wang, *Appl. Phys. Lett.* **79**, 3947 (2001).
- ⁴⁸G. Knuyt, L. De Schepper, and L. M. Stals, *Philos. Mag. B* **61**, 965 (1990); G. Knuyt, L. M. Stals, and L. De Schepper, *ibid.* **63**, 1289 (1991); G. Knuyt, and L. M. Stals, *ibid.* **64**, 299 (1991).
- ⁴⁹J. C. Dyre, *Phys. Rev. B* **75**, 092102 (2007).
- ⁵⁰G. Ruocco, F. Sette, R. Di Leonardo, G. Monaco, M. Sampoli, T. Scopigno, and G. Vilianni, *Phys. Rev. Lett.* **84**, 5788 (2000).