LETTER TO THE EDITOR

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Letter to the Editor

Extended elastic model for flow in metallic glasses

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ABSTRACT

We report that both shear and bulk moduli, not only shear modulus, are critical parameters involved in both homogeneous and inhomogeneous flows in metallic glass. The flow activation energy (ΔF) of various glasses when scaled with average molar volume V_m, which is defined as flow activation energy density $\rho_E = \Delta F/V_m$, can be expressed as: $\rho_E = \frac{10G + K}{11}$. The extended elastic model is suggestive for understanding the glass transition and deformation in metallic glasses.

The mysterious glass transition phenomenon, which connects the liquid and glassy states, has wide applications in daily life, industry, and organism preservation [1–4]. In the past decades, intensive efforts have been made to understand the glass transition [1,5–9]. To understand the flow in supercooled liquid and glass, many models have been proposed. The well-known models are the free volume model, the Adam–Gibbs entropy model, the mode-coupling theory and elastic models [1–6]. A successful model of viscous liquids and glasses must explain why the activation energy has such strong temperature dependence and can correlate the activation energy to simple and readily measurable parameter. Among these models, the elastic models link the glass transition and elastic moduli of the glasses [1]. All the elastic models link the activation energy to the readily measurable instantaneous shear modulus G. In metallic glasses, the glass transition temperature (T_g) indeed shows clear correlation with the elastic moduli such as Young's modulus E and G [10–18].

In this letter, based on the scaling laws between T_g and elastic moduli in metallic glasses, we demonstrate that the V_m scaled flow activation energy (ΔF), that is, flow activation energy density, $\rho_E = \Delta F/V_m$, is determined by both G and K in a way of $\rho_E = (10\,G + K)/11$. The physical origin of the extended elastic model is discussed. The temperature dependence of the viscosity of liquids approaching glass transition is [1]: $\eta = \eta_0 \exp\left[\frac{\Delta F(T)}{k_B T}\right]$, where, η_0 is a constant, and k_B is the Plank constant. At T_g, the viscosity of various liquids get to $\eta(T_g) = 10^{13}$ poise [3] for metallic glasses. For most metallic glasses the value delivers a good approximation for practical purposes, because most metallic glasses have similar fragility around T_g.

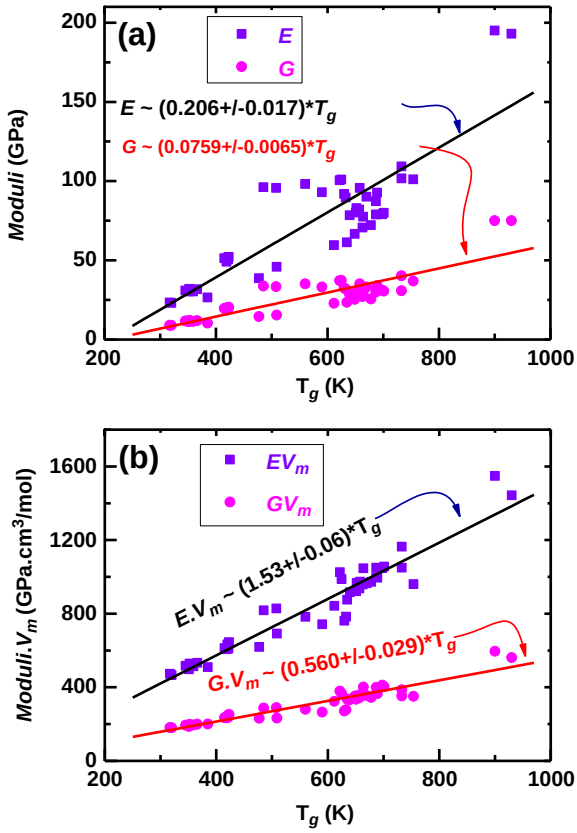

Fig. 1. (Color online) (a) Young's modulus E and shear modulus G of 46 kinds of metallic glasses vs T_g. (b) The combination of moduli and molar volume V_m vs T_g follows a better relationship. The solid lines are the linear fitting of the experimental data.

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Then, the $\Delta F/T_g$ should be the same for metallic glasses. A variety of elastic models have been proposed [1], which assume that ΔF is proportional to the elastic modulus [1], e.g. $\Delta F \propto G$. Fig. 1(a) shows experimental data of E and G vs T_g for 46 different kinds of bulk metallic glasses (BMGs) (listed in Table 1). These BMGs cover many typical alloy systems, including Zr-, Cu-, Ca-, Mg-, Ni-, Fe-, and rare earth element based BMGs, and their thermal, mechanical and physical properties are markedly different (Their values of T_g, E and Poisson's ratio span from 317 K to 930 K, 23 GPa to 195 GPa, 0.276 to 0.41, respectively) [12,13]. The linear fitting results are $E \propto (0.206 \pm 0.017)T_g$ and $G \propto (0.0759 \pm 0.0065)T_g$. The relations between T_g and G (and E) are key evidence for the elastic model [1], however, it can be seen that the data are rather scattered, and the adjusted R-square (the adjusted coefficients of determination [19]) are 0.755 and 0.741, respectively, which denotes that G or K should not be the only parameter that is involved in glass transition.

In fact, according to the shoving model, a characteristic volume V_c is involved in homogeneous flow of glass-forming liquids as [1,14]: $\Delta F = GV_c$. In inhomogeneous flow of glasses, the activation energy of a flow event unit (shear transformation zone, STZ) also correlates with volume as [15,16]: $\Delta F = (8/\pi^2)G\gamma_C^2\zeta\Omega$, where Ω is the volume of STZ and γ_C is the shear strain limit. Recently, it is found that the elastic moduli scaled with V_m show better correlations with the thermal and mechanical properties for metallic glasses [17,18,20,21]. Thus, the characteristic volume could be an important parameter involved in the flow event in glass transition and glass. Fig. 1(b) shows the plot of GV_m (and EV_m) vs T_g for these BMGs. Indeed, the data can be better fitted with $EV_m \propto (1.53 \pm 0.06)T_g$ and $GV_m \propto (0.560 \pm 0.029)T_g$, and the adjusted-R increases to 0.923 and 0.905, respectively. The results certify that the combination of G and V_m (E and V_m) does show much better correlation with T_g and the V_m is another important parameter in governing the glass transition.

It is found that the atom number N involved in the cooperative flow events of STZ in metallic glasses is similar and around ~100 [15,16], and the volume of STZ can be expressed as $V = \sum_{i=1}^{N\sim100} v_i = N\frac{V_m}{N_A}$ (where N_A is the Avogadro constant). The inhomogeneous flow in glass is a self-organized large number of local shearing events (or STZ) [15–17], and the transition from local shearing to macroscopic shear band results from the dramatic increase of the atom mobility and softening along a shear plane motivated by the input mechanical energy [15–17]. Thus, the transition is akin to a process of stress driven glass-to-liquid transition or glass transition [17]. Then, the involved

Table 1
The compositions, T_g, average molar volume V_m, K, E, G, ν, and the combined parameter *Moduli* $\cdot V_m/T_g$ of 46 different kinds of BMGs [11–21].

Compositions	T_g K	V_m cm^3/mol	K GPa	E GPa	G GPa	ν	GV_m/T_g	KV_m/T_g	$(0.91\,G+0.09\,K)V_m/T_g$
$Ca_{65}Mg_{8.54}Li_{9.96}Zn_{16.5}$	317	20.25	20.1	23.4	8.9	0.307	0.572	1.287	0.636
$Ca_{65}Mg_{8.31}Li_{9.69}Zn_{17}$	320	20.10	18.4	23.2	9.0	0.291	0.564	1.159	0.618
$Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$	385	19.24	19.8	26.5	10.4	0.276	0.520	0.989	0.562
$Ce_{70}Al_{10}Ni_{10}Cu_{10}$	359	16.94	27.0	30.3	11.5	0.314	0.543	1.274	0.609
$(Ce_{20}La_{80})_{68}Al_{10}Cu_{20}Co_2$	366	16.78	32.6	31.8	11.9	0.338	0.544	1.496	0.629
$Ce_{68}Al_{10}Cu_{20}Nb_2$	345	16.70	30.1	31.0	11.7	0.328	0.564	1.455	0.644
$(Ce_{80}La_{20})_{68}Al_{10}Cu_{20}Co_2$	355	16.69	31.8	31.1	11.6	0.337	0.547	1.494	0.632
$Ce_{68}Al_{10}Cu_{20}Co_2$	352	16.57	30.3	31.3	11.8	0.328	0.555	1.428	0.634
$Ce_{68}Al_{10}Cu_{20}Ni_2$	352	16.57	31.8	31.9	12.0	0.333	0.564	1.495	0.648
$Ce_{68}Al_{10}Cu_{20}Co_2$	351	16.44	30.1	30.3	11.5	0.333	0.532	1.411	0.611
$La_{60}Al_{20}Co_{20}$	477	15.96	39.2	38.7	14.5	0.335	0.486	1.311	0.560
$Pr_{55}Al_{25}Co_{20}$	509	15.07	43.5	45.9	15.4	0.341	0.456	1.287	0.531
$Dy_{55}Al_{25}Co_{20}$	635	14.27	52.2	61.4	23.5	0.304	0.529	1.174	0.587
$Tb_{55}Al_{25}Co_{20}$	612	14.15	50.2	59.5	22. 9	0.302	0.528	1.160	0.585
$Ho_{55}Al_{25}Co_{20}$	649	13.85	58.8	66.6	25.4	0.311	0.542	1.255	0.607
$Er_{55}Al_{25}Co_{20}$	663	13.55	60.7	70.7	27.1	0.306	0.553	1.241	0.615
$Tm_{39}Y_{16}Al_{25}Co_{20}$	664	13.51	66.1	77.5	29.7	0.305	0.604	1.345	0.671
$Tm_{55}Al_{25}Co_{20}$	678	13.47	62.0	72.2	25.6	0.319	0.509	1.232	0.574
$Lu_{39}Y_{16}Al_{25}Co_{20}$	687	13.30	71.3	78.9	30.0	0.316	0.581	1.380	0.653
$Lu_{45}Y_{10}Al_{25}Co_{20}$	698	13.25	70.2	79.1	31.1	0.307	0.590	1.332	0.657
$Lu_{55}Al_{25}Co_{20}$	701	13.20	69.2	80.0	30.6	0.307	0.576	1.303	0.642
$Mg_{65}Cu_{25}Gd_{10}$	421	12.51	45.1	50.6	19.3	0.313	0.573	1.340	0.642
$Mg_{65}Cu_{25}Y_9Gd_1$	423	12.37	39.0	52.2	20.4	0.277	0.597	1.142	0.646
$Mg_{65}Cu_{25}Y_{10}$	419	12.36	41.4	49.1	18.9	0.302	0.556	1.220	0.616
$Mg_{65}Cu_{25}Y_8Gd_2$	420	12.23	39.9	51.7	20.1	0.284	0.586	1.161	0.638
$Mg_{65}Cu_{25}Y_5Gd_5$	422	12.05	39.1	50.6	19.7	0.284	0.563	1.117	0.613
$Mg_{65}Cu_{25}Tb_{10}$	415	11.95	44.7	51.3	19.6	0.309	0.565	1.288	0.630
$Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$	640	11.68	106.6	78.4	28.5	0.377	0.519	1.946	0.648
$Zr_{65}Cu_{15}Ni_{10}Al_{10}$	652	11.65	106.7	83.0	30.3	0.37	0.541	1.906	0.664
$Zr_{61.88}Cu_{18}Ni_{10.12}Al_{10}$	651	11.51	108.3	80.1	29.1	0.377	0.514	1.915	0.640
$Zr_{55}Al_{19}Co_{19}Cu_7$	733	11.44	114.9	101.7	30.8	0.377	0.481	1.794	0.599
$Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$	687	11.44	107.7	87.3	32.0	0.365	0.533	1.793	0.646
$Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$	657	11.43	99.2	82.0	30.1	0.362	0.523	1.725	0.632
$(Zr_{59}Ti_6Cu_{22}Ni_{13})_{85.7}Al_{14.3}$	689	10.74	112.6	92.7	34.0	0.363	0.530	1.755	0.640
$Cu_{45}Zr_{45}Al_7Gd_3$	670	10.71	105.9	90.1	33.2	0.358	0.530	1.692	0.635
$Zr_{46.75}Ti_{8.25}Cu_{10.15}Ni_{10}Be_{27.25}$	622	10.21	111.9	100	37.2	0.35	0.610	1.836	0.721
$Zr_{48}Nb_8Cu_{12}Fe_8Be_{24}$	658	10.17	113.6	95.7	35.2	0.36	0.544	1.756	0.653
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	625	9.79	114.1	101	37.4	0.352	0.586	1.787	0.694
$Ni_{45}Ti_{20}Zr_{25}Al_{10}$	733	9.61	129.6	109	40.2	0.359	0.527	1.699	0.632
$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	754	9.50	128.2	101	36.9	0.369	0.465	1.616	0.569
$Pd_{77.5}Cu_6Si_{16.5}$	633	8.74	166.0	89.7	31.8	0.41	0.439	2.293	0.606
$Pd_{64}Ni_{16}P_{20}$	630	8.29	166.0	91.9	32.7	0.408	0.430	2.183	0.588
$Pd_{40}Cu_{40}P_{20}$	590	7.98	158.0	93.0	33.2	0.402	0.449	2.136	0.601
$Pd_{39}Ni_{10}Cu_{30}P_{21}$	560	7.97	159.1	98.2	35.1	0.397	0.500	2.264	0.658
$Fe_{53}Cr_{15}Mo_{14}Er_1C_{15}B_6$	900	7.94	180.0	195	75.0	0.317	0.610	1.588	0.698
$Fe_{61}Mn_{10}Cr_4Mo_6Er_1C_{15}B_6$	930	7.48	146.0	193	75.0	0.281	0.603	1.174	0.654

activation energy $GV = NGV_m/N_A$ should have a linear correlation with k_BT_g. The good linear correlation between GV_m (and EV_m) and T_g in Fig. 1(b) confirms that the N involved in the cooperative flow event for various metallic glasses is almost the same.

Based on above scaling laws and elastic model, we propose that it is the flow activation energy density (ρ_E), not the flow activation energy itself, that correlates with the elastic moduli as:

$$\rho_E = \frac{\Delta F}{V_m} \propto \text{Moduli}. \quad (1)$$

The extended elastic model means that the energy per volume needed in glass transition or in STZ in metallic glass is proportional to the elastic moduli.

Previous elastic models [1] suggest that the atoms or atomic groups go through pure shearing displacement which is independent of K, and the ρ_E depends only on G. Recent works [18,20] and the jamming model of granular systems [22] find that both shear and dilatation are involved in the flow during glass transition and deformation. Next, we further justify that the flow activation energy density ρ_E relates not to G or K but both G or K. That is, the flow event relates to both shearing transformation (corresponding to volume-preserving G) and dilatation (corresponding to volume-nonpreserving K). At T_g, the $\Delta F/T_g$ should be the same for all glasses that is independent of Poisson's ratio or other moduli [3]. However, the statistic analysis of both GV_m/T_g and KV_m/T_g for glasses listed in Table 1 linearly depends on ν as: $KV_m/T_g \propto 8.78\nu$ and $GV_m/T_g \propto -0.86\nu$, respectively [Fig. 2(a)–(b)]. The relationships between $\Delta F/T_g$ and ν should be neither the dashed black line (KV_m/T_g) nor the short-dashed olive line (GV_m/T_g) but a constant like the solid magenta line in Fig. 3(a). The slope in the relationship of KV_m/T_g vs ν is positive, while that of

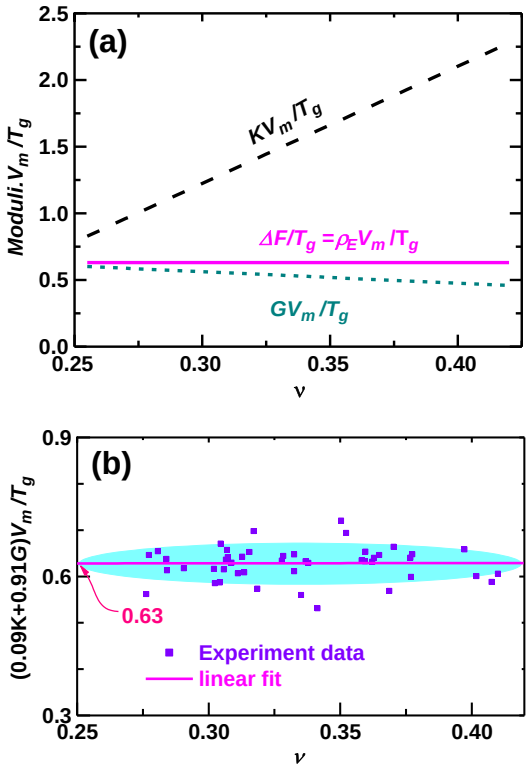

Fig. 3. (Color online) (a) Moduli · V_m/T_g vs ν. The black dashed line represents for KV_m/T_g vs ν, the dark cyan short-dashed line for GV_m/T_g vs ν, and the red solid line for ρ_E = Moduli which is Poisson's ratio independent. (b) The experiment data of $(0.91\,G + 0.09\,K)V_m/T_g$ vs ν are well linearly fitted, denoting that $(0.91\,G + 0.09\,K)$ V_m/T_g for various metallic glasses is independent of ν.

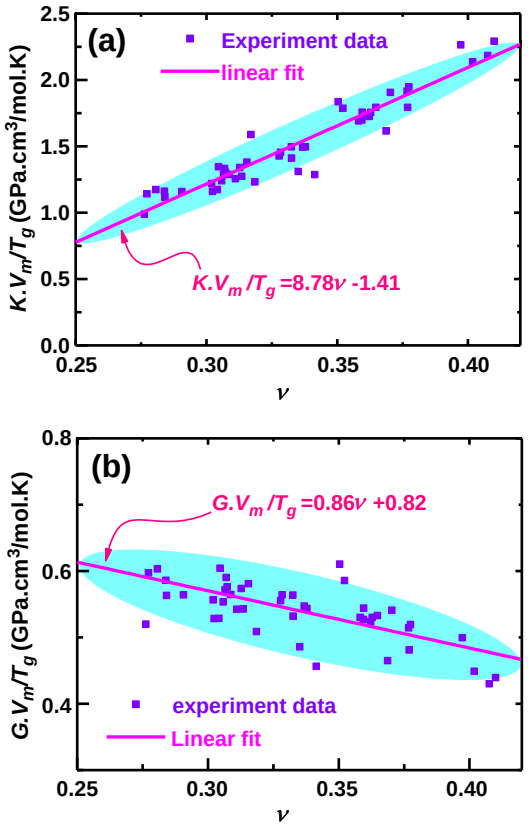

Fig. 2. (Color online) (a) KV_m/T_g vs Poisson's ratio ν and (b) GV_m/T_g vs ν for 46 kinds of metallic glasses. The lines are the linear fit of the experiment data.

GV_m/T_g vs ν is negative. The bigger the slope of KV_m/T_g vs ν (or GV_m/T_g vs ν) is, the less the contribution to ΔF of the modulus should be. This indicates that if $\Delta F/T_g$ would be a constant it should not only relate to G or K but a combination of both K and G. When the ratio of the contribution of G and K is about 8.78: $0.86 \approx 10{:}1$, or alternatively $\rho_E = \Delta F/V_m = (10\,G + K)/11$, the $\Delta F/T_g$ vs ν is a constant as shown in Fig. 3(a). Fig. 3(b) shows the results of $(0.91\,G + 0.09\,K)V_m/T_g$ vs ν for various BMGs. The data indeed can be well fitted by a constant of 0.63 and is independent of ν, which is consistent with the glass transition phenomenon that the viscosity of all the liquids gets to the same value at T_g. The $\Delta F = (0.91\,G + 0.09\,K)V_m$, which is independent of mass or amount, is a kind of elastic energy, and the ratio $\Delta F/RT_g = 0.63/R = 0.076$, which is dimensionless, can be regarded as some kind of elastic strain stored in a glassy state [23]. Thus, the glass transition could be regarded as the release or absorption of the elastic strain stored.

The acoustic velocity behaviors during glass transition further verify the extended elastic model. The T-dependent transversal (V_s) and longitudinal (V_L) velocities change differently during the glass transition process [1,24,25], and the ratio of their relative changes is about: $\frac{\Delta V_S}{V_S} : \frac{\Delta V_L}{V_L} \approx 2 : 1$. From $\rho V_S^2 = G$ and $\rho V_L^2 = \frac{4}{3}G + K$, we obtain that the relative changes of G and K in metallic glasses is: $\frac{\Delta G}{G} : \frac{\Delta K}{K} \approx 5 : 1$. In 3$D$ space, there are two shear models (corresponding to G) and one radial model (dilatation model corresponding to K) when atoms move. Thus, the contribution of G should be doubled, and the ratio of the contribution of G and K in ρ_E should be about 10:1, that is: $\rho_E = (10\,G + K)/11$.

We further discuss why the elastic moduli show better correlation with ρ_E rather than the activation energy itself. The shear elastic energy density ϕ of a STZ can be expressed as $\phi(\gamma) = \phi_0 \sin^2(\pi\gamma/4\gamma_C)$ [15], where ϕ_o is the total barrier energy density and γ is the shear

strain. The G can be reduced from the ϕ, not the shear elastic energy, in a way of $G=\phi''|_{\gamma=0}=\frac{\Phi_0}{8\gamma_C^2/\pi^2}$[15]. This indicates that G is related to the barrier energy density. The K can be expressed as $K = V_0\frac{\partial^2 U}{\partial V^2}|_{V=V_0} = \partial^2\left({}^{U}/_{V_0}\right)/\partial\left({}^{V}/_{V_0}\right)^2|_{V=V_0}$ [21], where U is the atomic potential energy, V_0 is the atomic equilibrium volume, U/V_0 is the energy density and V/V_0 correlates with elastic strain. In harmonic approximation around V_0, the U can be expressed in a parabolic form as $U=U_0(1-\alpha V/V_0)^2$ [1], where α is constant depending on the atomic bonding nature. This gives $K=2\alpha^2U_0/V_0$, which correlates with the potential energy density at an equilibrium state. Thus, both G and K are proportional to their corresponding deformation energy density. Therefore, it is reasonable for ρ_E rather than the activation energy shows correlation with the combination of K and G.

Most models for flow in glasses and supercooled liquids consider the case of simple shear, which involves only shear stress and shear modulus. Our model suggests that both homogeneous and inhomogeneous flows at one hand is a shearing process and on the other hand must generate free volume which is a form of dilatation (in fact, the shear induced dilatation has been widely observed [22]), and demonstrates that both shear and free volume are important for flow in glass transition and deformation, and provides an intuitional picture of the flow of the atoms or atomic groups in glass or liquid. Furthermore, the formation of shear bands when the BMGs deform plastically is thought to be akin to the process of glass transition [17,23]. Thus, this means that both the shear [26] and the dilatation [22] could be involved in the formation of shear bands. However, due to the critical difference between the two phenomena: the glass transition is constraint-free, while the formation of shear bands is stress-constraint, and the formation of shear bands then may involve less dilatation.

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