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The activation energy and volume of flow units of metallic glasses

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We report that the average activation energy and volume of flow units of metallic glasses can be measured by a dynamic mechanical analysis which is a sensitive tool for detecting atomic rearrangements associated with the flow “defects”. The obtained activation energy and volumes flow units of various metallic glasses are in agreement with that determined by other experimental methods and simulations. A correlation between the volume of plastic units and Poisson’s ratio of various metallic glasses is found.

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Intensive studies have been devoted to investigating the microscopic structural characteristics of metallic glasses (MGs) during glass transition and plastic deformation [1–7]. The structure of MGs can be considered as a random distribution of local regions of spatially fluctuating density, low viscosity and high entropy (and energy) in an atomically disordered continuum. Experimental evidence and simulations have shown the collective rearrangement processes when the temperature approaches the glass transition temperature (T_g) or applied stress is close to the yield stress [1–7]. The local cooperative motions of atoms acting as “flow units” originate from the structural heterogeneities or “potential flow defects” of MGs. Several phenomenological models have been proposed to describe the flow units, mainly based on two mechanisms: dilatation of free volume [2,3] and local events of cooperative shear motion of atomic clusters, termed shear transformation zones (STZs) [1,4–7]. Recently, a cooperative shearing model (CSM) [10] based on the concept of the potential energy landscape [8,9] was proposed to effectively interpret the plastic deformation of MGs well below T_g . The activation energy and volume (Ω) of flow units are key parameters for understanding the microscopic plastic mechanism, the structural heterogeneities and macroscopic mechanical properties of MGs. However, the activation energy and the volume of flow units are difficult to measure experimentally. Due to the disordered random structural characteristics of MGs, it is difficult to detect and identify the flow units. Therefore, little is known

about the activation energy, volume and number of atoms in a flow unit, and this hinders the in-depth understanding of the plastic deformation mechanism in MGs [2,11,12].

In this paper, we show that the activation energy W^* of flow units of MGs can be directly and simply determined by using dynamic mechanical analysis. The average volume of flow units and the number of atoms in a flow unit for various MGs are then experimentally obtained based on CSM theory. We also evaluate the relationship between the volume of the plastic units and the Poisson’s ratio, which is correlated with the mechanical properties of MGs [13,14].

Bulk MG samples were prepared by a copper mold suction casting method [15]. The glassy nature was identified by X-ray diffraction and differential scanning calorimetry. Dynamic mechanical analysis (DMA) was performed with a TA DMA Q800 instrument using a single-cantilever bending method for rod samples in a nitrogen-flushed atmosphere. The DMA experiments provided periodic deformation in the linear regime of MGs, with a maximum deformation of 10^{-5} . As a consequence, the properties of the MGs were not affected by the mechanical solicitation, and the deformation induced by the DMA is instantaneously recovered in MGs. The complex modulus: $E = E' + E''$, where E' is the storage modulus (elastic component) and E'' is the loss modulus (viscoelastic component), can be deduced by DMA. The E' and E'' were measured by temperature ramp mode at a heating rate of 3 K min^{-1} [15,16].

Dynamic mechanical spectroscopy is a sensitive tool for detecting atomic rearrangements associated with the flow “defects” of solids and the β relaxation [15,16].

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It has been well developed using DMA to characterize flow units in non-metallic glassy materials [17,18]. The structure of MGs can be considered as a random distribution of flow units in an atomically disordered continuum, as illustrated in Figure 1(a). Figure 1(b) show the loss modulus spectrum of MGs at 353 K (well below the T_g of 470 K), and the peaks in the spectrum is an internal loss peak corresponding to the loss tangents (internal friction peak) [17]. Note that the effect occurs in the elastic regime of the MGs, and is reversible. When the resonance condition is fulfilled, such that the frequency of the testing force is equal to the characteristic frequency of the deformation of the whole flow units, the possibility of rearrangement in flow units increases notably. These atomic rearrangements relate to the localized viscous flow within the flow units, which lead to the loss tangents of the system and show as internal loss peaks in the modulus spectrum. The characteristic frequency f display Arrhenius behavior: $f = f_0 \exp(W^*/RT)$, where f_0 is the frequency of vibration depending on activation entropy and W^* is the height of the energy barrier for the atomic movement in whole flow units, namely the activation energy for flow units [18]. Hence the activation energy of flow units can be obtained from the plot of $\ln(f)$ vs. $1/T$. Both the loss modulus as a function of temperature for different frequencies and the loss modulus as a function of frequency at different temperatures can be used to characterize the flow units and

determine the activation energy in glasses [16,19], as shown in Figure 2(a).

However, the DMA peaks responsible for the potential flow units of the known MGs are rather obscure [15]. They manifest as either broad humps or excess wings, and are closely merged into the glass transition. This makes it difficult to identify the flow units, or their correlations with mechanical properties, clearly. A new La-based MG system has recently been developed which shows an unprecedentedly strong internal friction peak in DMA measurements among the known MGs (see Fig. 2(b)). We can thus investigate the behavior of the flow units and determine their activation energy W^* by DMA.

According to CSM, the volume of plastic units (or STZ) Ω is proportional to W^* as [10]:

$$\Omega = W^* / (8/\pi^2) \gamma_c^2 \zeta G \quad (1)$$

where constant $\zeta \approx 3$ is a correction factor arising from the matrix confinement of a “dressed” flow units (or STZ) [20], $\gamma_c \approx 0.027$ is the average elastic limit, Ω is the volume of flow units and G is shear modulus.

Based on the random dense packing model, Falk and Langer [2] proposed that the flow unit volume can be expressed as: $\Omega = n C_f V_a$, where n is the number of atoms in a flow unit and the constant $C_f (\approx 1.1)$ is a free volume parameter [2]. V_a is the atomic volume, which can be

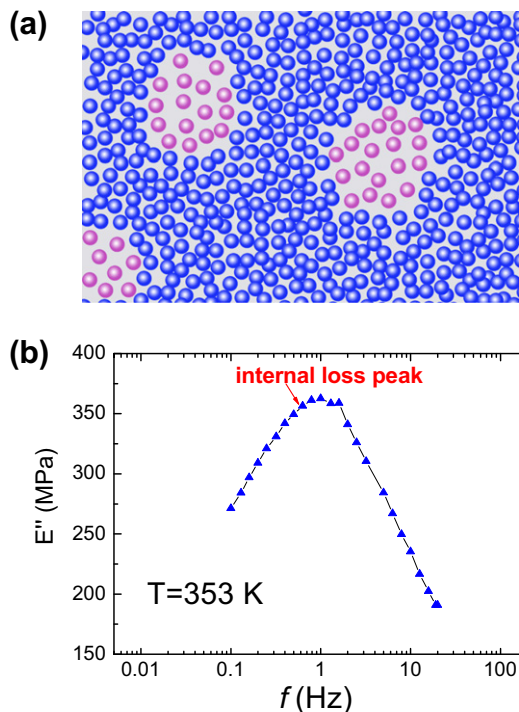


Figure 1. (a) Illustration of flow units in MGs. The MGs can be considered as a random distribution of flow units (regions with pink atoms) in an atomically disordered continuum. (b) The loss modulus spectrum of $\text{La}_{60}\text{Al}_{25}\text{Ni}_{15}$ MG measured at 353 K. The peaks in the spectrum are a kind of internal loss peak, and correspond to the internal friction peak. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

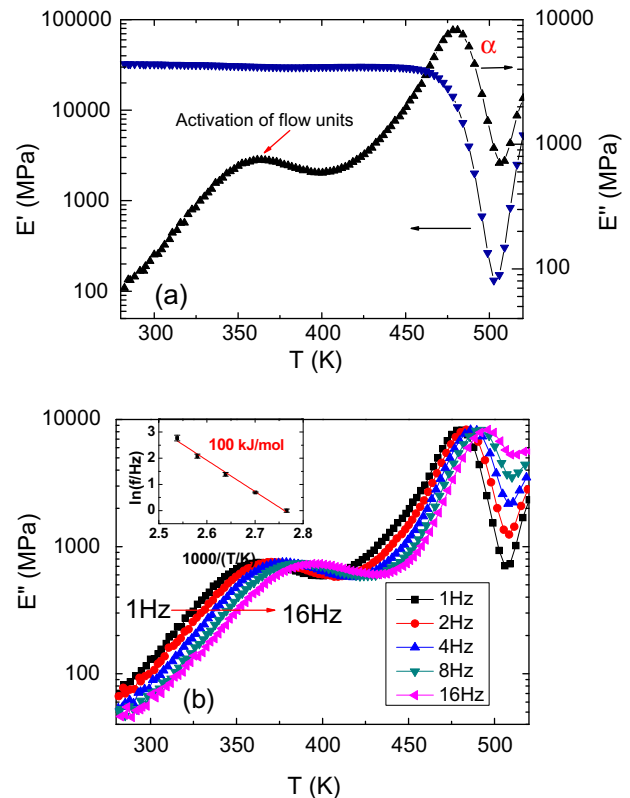


Figure 2. (a) The loss modulus E'' and storage modulus E' vs. T of $\text{La}_{60}\text{Al}_{25}\text{Ni}_{15}$ MG measured at 1 Hz. (b) The loss modulus E'' vs. T of $\text{La}_{60}\text{Al}_{25}\text{Ni}_{15}$ MG with f range of 1–16 Hz. The peak representing the flow units can be clearly distinguished from the glass transition (α relaxation) peaks. The inset figure is a plot of $\ln(f)$ vs. $1000/T_{fr}$.

expressed as $V_a = M/(\rho N_0)$, where ρ is the density, M is the molar mass and N_0 is the Avogadro constant. Hence, one can estimate the number of atoms in a flow unit of MGs as:

$$n = \Omega \rho N_0 / (C_f M) \quad (2)$$

The DMA spectrum of an $\text{La}_{60}\text{Al}_{25}\text{Ni}_{15}$ MG is used to show the determination of W^* . Figure 2(a) shows plots of E'' and E' vs. T of the $\text{La}_{60}\text{Al}_{25}\text{Ni}_{15}$ MG measured at 1 Hz. For the E'' curve, in addition to the α relaxation peak around 480 ± 5 K, a distinct broad peak around 361 ± 3 K can also be observed. The loss modulus spectrum peak corresponds to the internal friction of the heterogeneities of microstructure or the “defects” of MG (potential flow units) [15,16,21–23]. Both the glass transition (or α relaxation) and activation of the flow units correspond to a drop in the E' curve. Thereafter, only E'' is used to characterize the potential flow units.

Figure 2(b) shows the shift in the peaks of E'' curve depending on the changing frequency. As the frequency increases from 1 to 16 Hz, the peak moves towards higher temperature. W^* can be obtained from the plot of $\ln(f)$ vs. $1000/T_{fu}$ (inset plot in Fig. 2(b)), where T_{fu} is the peak temperature of the activation of flow units. One can see from the inset that the $\ln(f)$ vs. $1000/T_{fu}$ plot follows the Arrhenius type well, which is the characteristic of the activation of flow units [18]. From the slope of the linear fitting, we obtain $W^* = 100 \text{ kJ mol}^{-1}$ for $\text{La}_{60}\text{Al}_{25}\text{Ni}_{15}$ MG. For the $\text{La}_{60}\text{Al}_{25}\text{Ni}_{15}$ MG, the shear modulus G is 17.0 GPa. Based on Eqs. (1) and (2), the Ω and n of the $\text{La}_{60}\text{Al}_{25}\text{Ni}_{15}$ MG are estimated to be $5.50 \pm 0.10 \text{ nm}^3$ and 178 ± 10 , respectively.

Note that for some MGs, such as the intermediate or strong glasses [24,25], the activation of flow units is often manifested as humps or unapparent excess wings rather than pronounced relaxation peaks. In these cases, the DMA method can also be applied to determine their flow unit activation [26].

We measured and collected the data of W^* determined from DMA and the shear modulus G for 20 typical MGs of six different systems. The data are presented in Table 1 [25]. The activation energy and average volume of flow units for these MGs were estimated and are also presented in Table 1. The obtained flow unit volumes of the various MGs range from 2.36 to 6.18 nm^3 , which is in good agreement with those accessed by experimental measurements and simulations [11,12,27]. From the obtained flow units volume and Eq. (2), we can further estimate the number of atoms in a flow unit for various MGs. The obtained values of n for various MGs, ranging from about 170–250, are also presented in Table 1. The results are in good agreement with those reported in previous research by theoretical prediction [10] and MD simulations [12].

The flow units accommodate the plastic deformation in MGs [2,4]. Microscopically, when MGs are subject to stresses (below yield stress) or thermal activation (below glass transition temperature), some nanoscale soft regions with low density and high friction of free volumes are activated and become flow units; this represents the local reversible rearrangement of atomic configuration under stress. When the applied stress is larger than yield stress, the flow units will overcome the energy barrier and become irreversible. The cooperative shearing and percolation of the plastic events lead to the macroscopic plastic deformation [28].

Since Ω is the key parameter for characterizing the flow units and is closely related to the plastic deformation of MGs, we looked at the relationship between the average flow units volume Ω and Poisson's ratio ν . As an indicator of plasticity of MGs, Poisson's ratio, which is equivalent to the ratio of K/G , has been found to have a clear correlation with plasticity of a MG, and the correlation widely used for exploring plastic metallic glasses [13]. In the plasticity and ν correlation, there exists a critical value of ν ($=0.34$) that divides plasticity from brittleness of various MGs. Below 0.34 or values

Table 1. The activation energy of W^* (some data are from Refs. [15,26]), volume Ω , number of atoms n in a flow unit, shear modulus G [25], Poisson's ratio ν [25] and atomic volume of various metallic glasses.

Metallic glass	W^* (kJ mol ⁻¹)	G (GPa)	ν	Ω (nm ³)	V_a (Å ³)	n
$\text{La}_{50}\text{Al}_{35}\text{Ni}_{15}$	110	19.6	0.328	5.27	–	–
$\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$	110	19.4	0.326	5.31	–	–
$\text{La}_{60}\text{Al}_{25}\text{Ni}_{15}$	100	17.0	0.325	5.50	28.08	178
$\text{La}_{70}\text{Al}_{15}\text{Ni}_{15}$	93	17.4	0.324	5.03	–	–
$\text{La}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{10}\text{Co}_{15}$	89	15.6	0.342	5.37	–	–
$\text{La}_{57.5}\text{Cu}_{12.5}\text{Ni}_{12}\text{Al}_{18}$	88	13.5	0.330	6.13	–	–
$\text{La}_{57.5}(\text{Cu}_{50}\text{Ni}_{50})_{25}\text{Al}_{17.5}$	92	14.0	0.348	6.18	27.73	203
$\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$	118	35.3	0.355	3.13	16.53	172
$\text{Zr}_{57}\text{Cu}_{15.4}\text{Ni}_{12.6}\text{Al}_{10}\text{Nb}_5$	135	32.0	0.365	3.95	18.88	190
$\text{Zr}_{53.7}\text{Cu}_{28.5}\text{Ni}_{9.4}\text{Al}_{8.4}$	133	29.8	0.372	4.18	18.64	204
$\text{Zr}_{64.13}\text{Cu}_{15.75}\text{Ni}_{10.12}\text{Al}_{10}$	112	28.9	0.377	3.63	19.47	169
$\text{Zr}_{65}\text{Cu}_{15}\text{Ni}_{10}\text{Al}_{10}$	131	28.9	0.377	4.24	20.57	187
$\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$	129	34.5	0.399	3.50	13.19	241
$\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$	106	35.5	0.404	2.80	–	–
$\text{Pd}_{48}\text{Ni}_{32}\text{P}_{20}$	92	36.5	0.400	2.36	–	–
$\text{Cu}_{45}\text{Zr}_{45}\text{Al}_{10}$	153	36.3	0.364	3.95	17.04	211
$(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$	174	34.3	0.366	4.75	17.22	251
$\text{Cu}_{47}\text{Zr}_{47}\text{Al}_6$	155	33.8	0.367	4.29	17.39	224
$\text{Tm}_{39}\text{Y}_{16}\text{Al}_{25}\text{Co}_{20}$	151	29.7	0.304	4.76	22.44	193
$\text{Al}_{82}\text{Ni}_{10}\text{Ce}_8$	158	25.9	0.324	5.71	–	–

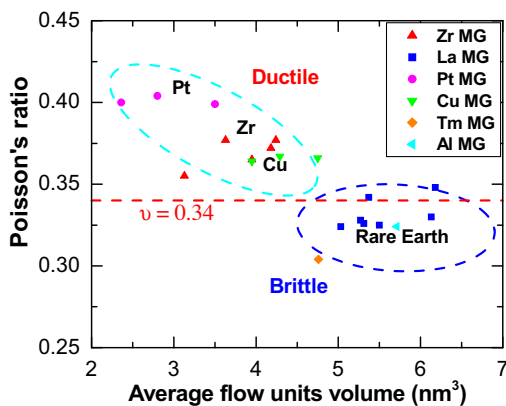


Figure 3. The STZ volume vs. Poisson's ratio ν for various metallic glasses listed in Table 1. The horizontal dash line denotes the boundary between brittle and ductile MGs.

for K/G less than approximately 2.5, the MGs exhibit brittle behavior, and higher values of ν give better plasticity [13]. The statistical survey of flow units volume vs. Poisson's ratio ν applied to six typical kinds of MG systems is shown in Figure 3. In different MGs systems, as the value of Ω increases from 2.36 to 6.18 nm³, the value of ν drops fast, from 0.404 to 0.304. Interestingly, one can see that a similar trend of MGs with smaller Ω having bigger ν exists even in the same MG system with a slight change of components. One can see that the MGs with smaller values of Ω (such as Pt-, Zr- and Cu-based MGs [29–31]) have larger values of ν and also better plasticity, while those with larger values of Ω (such as rare earth-based MGs) have smaller values of ν and poor plasticity. This is consistent with the plasticity and Poisson's ratio correlation. The formation of a shear band in MGs is due to the local collection of flow units. The global plasticity can be triggered when the high-density potential flow units are activated to reach the percolation limit and high-density multiple shear bands are formed by stress. A small flow unit volume (such as in the Pd-, Zr- and Cu-based MGs), when compared with a larger one (such as in Tm- and Al-based MGs), enables more flow units to be activated for the nucleation of more shear bands, and promotes the formation of multiple shear bands and larger plasticity in MGs. We also note that the correlation between Poisson's ratio and the size of flow units shown in Figure 3 resembles that between Poisson's ratio and the molar volume (shown in Fig. 57 of Ref. [25]). However, the molar volume is a macroscopic parameter determined by density measurement, while the flow unit volume is a microscopic parameter determined by the DMA method. Their underlying reasons and implications of the similar change tendency vs. Poisson's ratio are not clear; these will be the focus of our future work.

In summary, we show that the DMA can effectively evaluate the activation energy and volume of plastic units of MGs based on the CSM theory. The activation energy, volume of flow units and the number of atoms in flow units for various MGs have been obtained. The

volume of flow units is found to correlate with the Poisson's ratio and is related to the ductility of MGs – which provides a useful microstructural insight into the origins of the correlation between Poisson's ratio and plasticity, and the mechanisms of plastic deformation of metallic glasses. The results might be helpful for the design of ductile metallic glasses.

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- [1] F. Spaepen, *Acta Metall.* 25 (1977) 407.
- [2] M.L. Falk, J.S. Langer, *Phys. Rev. E* 57 (1998) 7192.
- [3] F. Spaepen, D. Turnbull, *Scripta Metal.* 8 (1974) 563.
- [4] A.S. Argon, *Acta Metall.* 27 (1979) 47.
- [5] H.L. Peng, M.Z. Li, W.H. Wang, *Phys. Rev. Lett.* 106 (2011) 135503.
- [6] E. Bouchbinder, J.S. Langer, I. Procaccia, *Phys. Rev. E* 75 (2007) 036107.
- [7] P. Schall, D.A. Weitz, F. Spaepen, *Science* 318 (2007) 1895.
- [8] F.H. Stillinger, T.A. Weber, *Science* 267 (1995) 1935.
- [9] P.G. Debenedetti, F.H. Stillinger, *Nature (London)* 410 (2001) 259.
- [10] W.L. Johnson, K. Samwer, *Phys. Rev. Lett.* 95 (2005) 195501.
- [11] D. Pan, A. Inoue, T. Sakurai, M.W. Chen, *Proc. Natl. Acad. Sci. USA* 105 (2008) 14769.
- [12] S.G. Mayr, *Phys. Rev. Lett.* 97 (2006) 195501.
- [13] J.J. Lewandowski, W.H. Wang, A.L. Greer, *Philos. Mag. Lett.* 85 (2005) 77.
- [14] X.F. Liu, R.J. Wang, W.H. Wang, *Scripta Mater.* 62 (2010) 254.
- [15] Z. Wang, H.B. Yu, P. Wen, H.Y. Bai, W.H. Wang, *J. Phys.: Condens. Matter* 23 (2011) 142202.
- [16] Z.F. Zhao, P. Wen, C.H. Shek, W.H. Wang, *Phys. Rev. B* 75 (2007) 174201.
- [17] J.Y. Cavallé, J. Perez a, *Phys. Rev. B* 39 (1989) 2411.
- [18] J. Perez, J.Y. Cavallé, *J. Non-Cryst. Solids* 172–174 (1994) 1028.
- [19] K.L. Ngai, S. Capaccioli, *Phys. Rev. E* 69 (2004) 031501.
- [20] J.S. Harmon, M.D. Demetriou, W.L. Johnson, K. Samwer, *Phys. Rev. Lett.* 99 (2007) 135502.
- [21] K.L. Ngai, M. Paluch, *J. Chem. Phys.* 120 (2004) 857.
- [22] B. Zhang, D.Q. Zhao, M.X. Pan, W.H. Wang, A.L. Greer, *Phys. Rev. Lett.* 94 (2005) 205502.
- [23] J.C. Ye, J. Lu, C.T. Liu, Q. Wang, Y. Yang, *Nat. Mater.* 9 (2010) 619.
- [24] C.A. Angell, K.L. Ngai, G.B. McKenna, P.F. McMillan, S.W. Martin, *J. Appl. Phys.* 6 (2000) 3113.
- [25] W.H. Wang, *Prog. Mater. Sci.* 57 (2011) 487.
- [26] H.B. Yu, W.H. Wang, H.Y. Bai, Y. Wu, M.W. Chen, *Phys. Rev. B* 81 (2010) 220201.
- [27] Y. Wu, G.L. Chen, X.D. Hui, C.T. Liu, Y. Lin, X.C. Shang, Z.P. Lu, *J. Appl. Phys.* 106 (2009) 083512.
- [28] C.A. Schuh, T.C. Hufnagel, U. Ramamurty, *Acta Mater.* 55 (2007) 4067.
- [29] J. Schroers, W.L. Johnson, *Phys. Rev. Lett.* 93 (2004) 255506.
- [30] Y.H. Liu, G. Wang, D.Q. Zhao, W.H. Wang, *Science* 315 (2007) 1385.
- [31] J. Das, M.B. Tang, K.B. Kim, R. Theissmann, F. Baier, W.H. Wang, J. Eckert, *Phys. Rev. Lett.* 94 (2005) 205501.