

## Deformation of glass forming metallic liquids: Configurational changes and their relation to elastic softening

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The change in the configurational enthalpy of metallic glass forming liquids induced by mechanical deformation and its effect on elastic softening is assessed. The acoustically measured shear modulus is found to decrease with increasing configurational enthalpy by a dependence similar to one obtained by softening via thermal annealing. This establishes that elastic softening is governed by a unique functional relationship between shear modulus and configurational enthalpy. © 2007 American Institute of Physics. [DOI: 10.1063/1.2717017]

In the recent work of Johnson and co-workers,<sup>1–4</sup> a link between elastic softening and configurational changes in metallic glass forming liquids has been proposed. The steepness of the viscosity dependence on temperature in the vicinity of the glass transition, i.e., the liquid fragility, has been known to be associated with the stored configurational enthalpy since the early work of Angell and co-workers.<sup>5–7</sup> Furthermore, the effect of strain rate on viscosity induced by mechanical deformation has also been linked to changes in configurational enthalpy.<sup>8</sup> However, attributing the deformationally induced softening of liquids to a unique functional relation between shear modulus and stored configurational enthalpy is a concept that has just recently been brought to attention.<sup>3</sup> This concept essentially suggests that conversion of mechanical work into stored configurational enthalpy induces softening via a dependence of shear modulus on configurational enthalpy. The thermodynamic state variable controlling flow in this concept is identified to be the isoconfigurational shear modulus. Experimental validation of earlier concepts based on the “free volume” hypothesis<sup>9</sup> has not been possible, mainly due to the lack of a fundamental thermodynamic definition of free volume. In contrast, the isoconfigurational shear modulus is a thermodynamically well-defined and experimentally accessible property, rendering this concept experimentally verifiable. In the present study, the change in configurational enthalpy induced by mechanical work and its effect on the softening of metallic glass forming liquids is evaluated by means of compressive experiments, ultrasonic measurements, and enthalpy recovery tests.

For the loading experiments we utilized cylindrical specimens of  $\text{Pt}_{57.2}\text{Ni}_{5.3}\text{Cu}_{14.7}\text{P}_{22.5}$  (Refs. 10 and 11) and  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ ,<sup>3,12</sup> which we deformed isothermally at constant strain rates. The loading setup described in Ref. 13 is utilized. Deformation was performed for a period of time sufficient to allow a steady flow stress state in the non-Newtonian regime to be attained. Upon unloading, the specimens were quenched as rapidly as possible to capture the configurational state associated with that flow stress.

We assessed the elastic softening induced by mechanical deformation by evaluating the isoconfigurational shear modulus at the high-frequency “solidlike” limit  $G$ . We evaluated  $G$  of the quenched unloaded specimens ultrasonically,<sup>14</sup> and extrapolated the room temperature measurements to estimate  $G$  at the temperatures of the flow experiments using linear Debye-Grüneisen coefficients, hence accounting for the thermal expansion effect on  $G$ . Shear longitudinal wave speeds were measured using the pulse-echo overlap setup described in Ref. 2. Densities were measured by the Archimedes method, as given in Ref. 15. The configurational changes induced by mechanical deformation were assessed by evaluating the configurational enthalpy stored in the deformed specimens  $\Delta h$ , taken as the change in the recovered enthalpy in reference to a relaxed undeformed state.<sup>16</sup> Differential scanning calorimetry (DSC) was employed using a Netzch DSC 404C at a scan rate of 10 K/min. The dependence of  $G$  on  $\Delta h$  is assessed by plotting the measured shear modulus against the recovered enthalpy.

We investigated the effect of isothermal constant strain rate deformation on  $G$ . We deformed two  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$  specimens, both at a temperature of 548 K and a strain rate of  $10^{-4} \text{ s}^{-1}$ . One of the specimens was at the as-cast nonequilibrium state, while the other had been previously relaxed by annealing at 548 K for 50 h. The stress-strain responses are shown in Fig. 1. Both specimens are shown to undergo a transient relaxation response toward a steady nonequilibrium flow stress state. While the stress overshoots during relaxation are dramatically different for the two specimens (a consequence of different initial structural states), the steady flow stress states are very similar. This demonstrates that the steady flow stress state at a given temperature and strain rate is unique, independent of the initial structural state. The relaxation process exemplified by the transient stress-strain responses constitutes a general relaxation process for all material properties, including  $\Delta h$  and  $G$ . The measured shear moduli for each specimen before and after deformation are presented in the inset of Fig. 1. As expected, prior to deformation the shear modulus of the relaxed specimen is higher than that of the as-cast specimen (a consequence of the relaxed specimen being at a lower-energy equilibrium state). After deformation, the shear modulus of the relaxed specimen relaxes to a lower steady value, while the shear modulus

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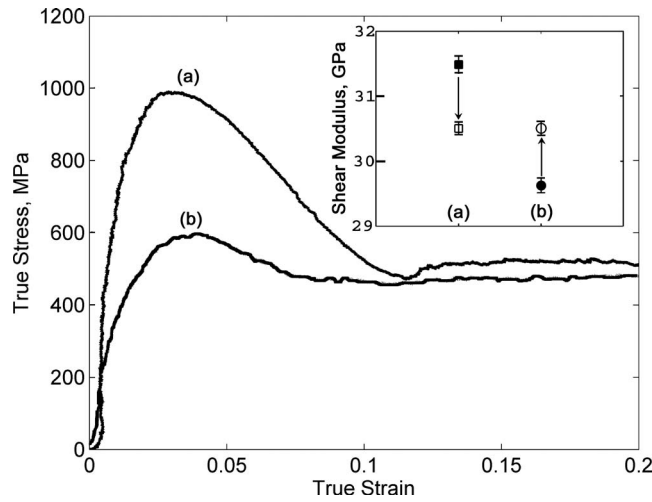


FIG. 1. True stress-strain curves for two  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$  specimens deformed at 548 K and a strain rate of  $1.0 \times 10^{-4} \text{ s}^{-1}$ : (a) specimen was relaxed at 548 K prior to deformation and (b) specimen was in the as-cast state. Inset: (a) shear modulus of the relaxed specimen before (■) and after deformation (□) and (b) shear modulus of the as-cast specimen before (●) and after deformation (○).

of the as-cast specimen relaxes to a higher steady value. The postdeformation shear moduli are nearly identical. We have demonstrated that the unique steady nonequilibrium state attained under a given flow stress is associated with a unique steady-state  $G$ .

Since the steady state is independent of the initial state, we chose to proceed using as-cast specimens since they are at a higher initial energy state allowing a greater range of strain rates for homogeneous flow. In Fig. 2 we present the stress-strain responses of  $\text{Pt}_{57.2}\text{Ni}_{5.3}\text{Cu}_{14.7}\text{P}_{22.5}$  and  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ , deformed at the indicated strain rates, and temperatures of 473 and 548 K, respectively, slightly below the respective calorimetric glass transition temperatures of 500 and 577 K (at 20 K/min scans). As noticed from Figs. 1 and 2, the transient relaxation process is completed at a strain of 0.10–0.11 in all tests. This strain limit, which can be observed in essentially all mechanical tests performed in metallic glass forming liquids, should be associated with individual barrier crossing events of shear transformation zones. The configurational strain (shear strain between saddles in configurational space) is found to be 0.036 for all metallic glass forming systems.<sup>1</sup> Therefore, a single barrier crossing event would be associated with a shear strain of  $4 \times 0.036$ , equivalent to a uniaxial strain of  $\sim 0.105$  (for Poisson's ratio of  $\sim 0.37$ ). Once steady state is attained at this critical strain, configurational changes cease and essentially all of the mechanical work is dissipated as heat.

In Fig. 3 we present DSC traces for the deformed specimens as well as the undeformed relaxed specimens. The configurational enthalpies stored at each steady state were evaluated from the DSC traces. The shear moduli of the deformed specimens associated with the respective steady flow states were measured acoustically and corrected for the Debye-Grüneisen effect. We utilized measured linear Debye-Grüneisen coefficients of 13 MPa/K for  $\text{Pt}_{57.2}\text{Ni}_{5.3}\text{Cu}_{14.7}\text{P}_{22.5}$  (Ref. 17) and 15 MPa/K for  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ .<sup>18</sup> To evaluate the thermodynamic dependence of  $G$  on  $\Delta h$ , we plot their respective values in Fig. 4. As evidenced from this plot,  $G$  decreases with increasing  $\Delta h$  in an approximately linear fashion. This dependence of  $G$  on  $\Delta h$  is supported by mo-

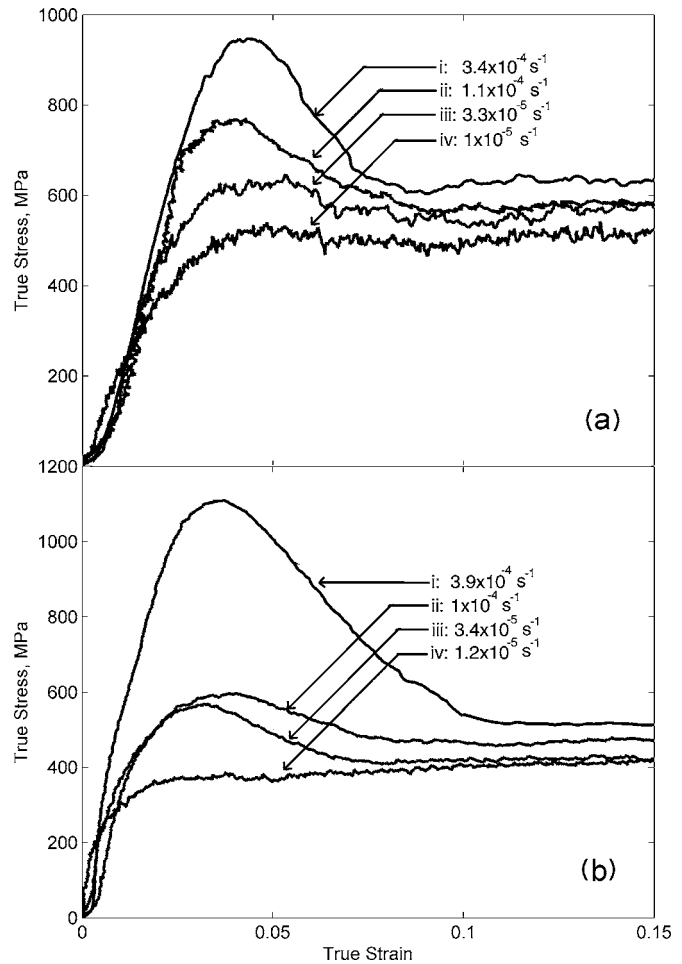


FIG. 2. True stress-strain diagrams for (a)  $\text{Pt}_{57.2}\text{Ni}_{5.3}\text{Cu}_{14.7}\text{P}_{22.5}$  at 473 K and (b)  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$  at 548 K at the indicated strain rates.

lecular dynamics simulations,<sup>4</sup> and suggests that the elastic softening induced by mechanical deformation is governed by the dependence of  $G$  on  $\Delta h$ .

We argue that the dependence of  $G$  on  $\Delta h$  obtained here by mechanically deforming the liquid is a unique functional relation. We can validate this argument by comparing this dependence against one obtained via a different softening path. One such path can be realized by inducing softening via annealing at incrementally higher temperatures, as performed in Ref. 2. From separate thermal annealing studies, we find  $dG/dT \approx -80 \text{ MPa/K}$  for  $\text{Pt}_{57.2}\text{Ni}_{5.3}\text{Cu}_{14.7}\text{P}_{22.5}$  (Ref. 10) and  $\approx -45 \text{ MPa/K}$  for  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ .<sup>19</sup> We further utilize  $d\Delta h/dT = 2.56 \text{ MJ/m}^3 \text{ K}$  for  $\text{Pt}_{57.2}\text{Ni}_{5.3}\text{Cu}_{14.7}\text{P}_{22.5}$  and  $1.95 \text{ MJ/m}^3 \text{ K}$  for  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$  (from the present DSC scans with  $d\Delta h/dT$  taken as the change in heat capacity at the glass transition temperature). Therefore for thermal annealing experiments  $dG/d\Delta h = (dG/dT)/(d\Delta h/dT)$ , can be calculated to be  $\approx -31.3$  for  $\text{Pt}_{57.2}\text{Ni}_{5.3}\text{Cu}_{14.7}\text{P}_{22.5}$  and  $\approx -23.1$  for  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ . For the present mechanical deformation experiments  $dG/d\Delta h$  is calculated from Fig. 3 as  $\approx -31.0$  for  $\text{Pt}_{57.2}\text{Ni}_{5.3}\text{Cu}_{14.7}\text{P}_{22.5}$  and  $\approx -22.7$  for  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ . We have thus shown that  $dG/d\Delta h$  realized by thermally annealing the liquid is approximately equivalent to  $dG/d\Delta h$  realized by mechanically deforming the liquid. We therefore conclude that the dependence of  $G$  on  $\Delta h$  is a unique functional relation.

In conclusion, we evaluated the changes in the configurational enthalpy of metallic glass forming liquids induced

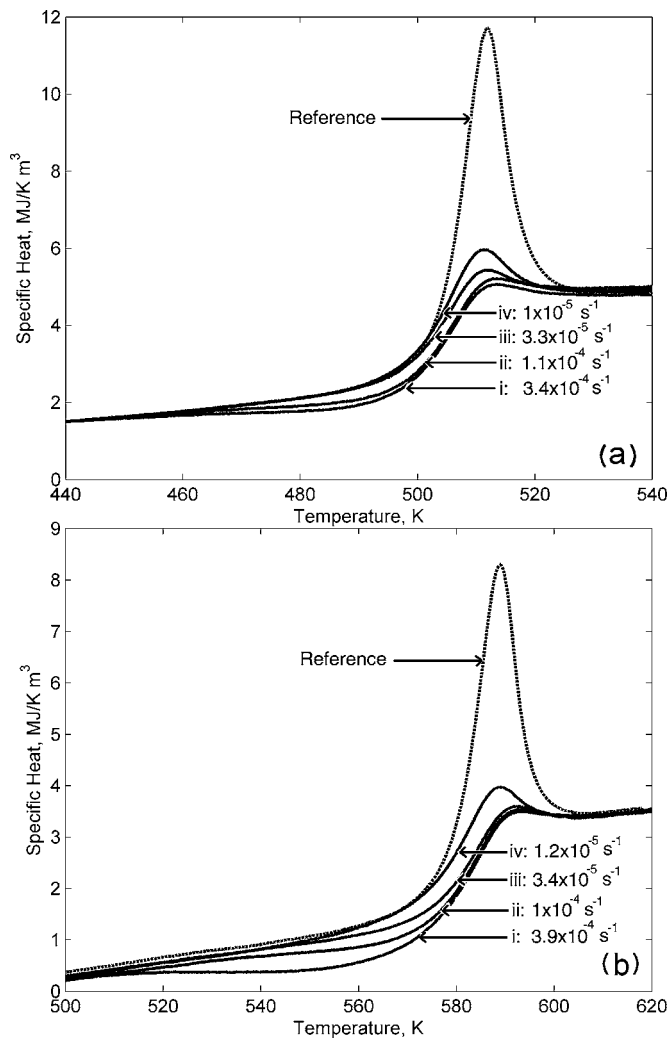


FIG. 3. DSC traces obtained from the deformed as well as undeformed relaxed specimens for (a) Pt<sub>57.2</sub>Ni<sub>5.3</sub>Cu<sub>14.7</sub>P<sub>22.5</sub> and (b) Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub>. The loading strain rates are indicated.

by mechanical deformation and assessed their effect on elastic softening. We found that the isoconfigurational shear modulus decreases with increasing configurational enthalpy in an approximately linear trend, in agreement with recent molecular dynamics simulations. By recognizing that an equivalent dependence of shear modulus on configurational enthalpy arises via a thermal softening path, we have established that this dependence is essentially a unique functional relation.

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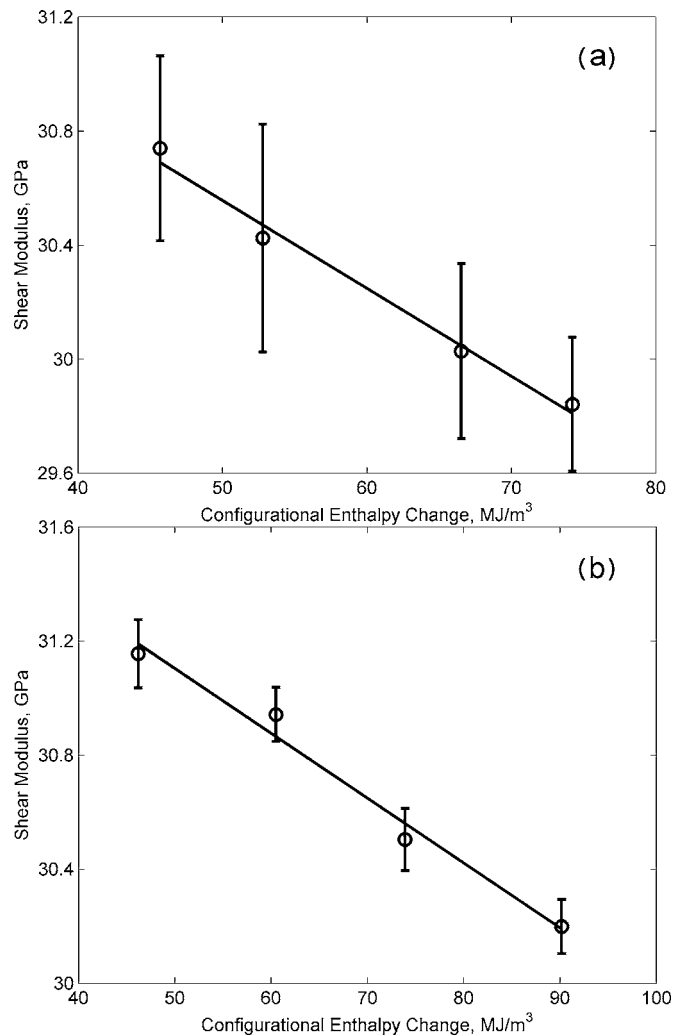


FIG. 4. Isoconfigurational shear modulus vs configurational enthalpy change for each steady flow state for (a) Pt<sub>57.2</sub>Ni<sub>5.3</sub>Cu<sub>14.7</sub>P<sub>22.5</sub> and (b) Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub>. The dotted lines are linear regressions to the data.

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