

Isoconfigurational Elastic Constants and Liquid Fragility of a Bulk Metallic Glass Forming Alloy

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Samples of $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ were isothermally annealed and quenched near the glass transition temperature and studied by the pulse-echo overlap technique. The shear modulus G of the samples shows a strong reversible dependence on annealing temperatures and, thus, on the specific configurational potential energy of the equilibrium liquid. The low- T dependence of G of the configurationally frozen glasses shows linear temperature dependence as expected by Debye-Grüneisen theory. The T dependence of G in the liquid state is directly related to the viscosity and fragility of the liquid.

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In the past 20 years, many multicomponent alloys that form bulk metallic glasses (BMGs) have been found [1–5]. Zirconium-based BMGs are highly processable and are utilized commercially for items such as sporting goods, surgical instruments, and strong, thin cases for electronic devices. In the undercooled melt, Zr-based alloys exhibit “strong” liquid behavior with an Angell fragility of $m \sim 30$ [6,7].

The enthalpy recovery method has been used in relaxation experiments to determine the enthalpy of the equilibrium liquid $h_L(T)$ around the glass transition temperature [8,9]. According to the potential energy landscape (PEL) or inherent state (IS) theory of Stillinger and later refinements, the liquid enthalpy consists of separate vibrational and configurational contributions $h_L = h_V + h_C$ [10,11]. The glass transition can be identified with the configurational freezing of inherent states. The glass or liquid heat capacity anomaly at the glass transition temperature T_g , $\Delta c_P = c_P^L - c_P^G$, can be directly associated with the configurational enthalpy $h_C(T)$ so that $h_C(T) \approx h_C(T_g) + \Delta c_P(T - T_g) +$ higher order terms. By contrast, the vibrational enthalpy is expected to vary smoothly as the glass transition is traversed. Recently, Johnson and Samwer developed a cooperative shear model to describe plastic yielding of metallic glasses in the glassy state below T_g [12]. The barrier W for shear flow is related by a scaling law to a universal critical yield strain γ_{C0} , the shear modulus G for a fixed glass configuration, and the effective volume of cooperative shear zones (CSZ) $\Omega_{\text{eff}} = \zeta\Omega$.

$$W = \left(\frac{8}{\pi^2}\right)G\gamma_{C0}^2\zeta\Omega. \quad (1)$$

The core volume of CSZ is Ω , and ζ is an “Eshelby” factor correcting for matrix confinement of the CSZ. This relation predicts that the barrier height for shear flow for a given glass or liquid configuration is proportional to G . For an equilibrium liquid near and above T_g , the IS configuration and corresponding configurational enthalpy depend on T . It is natural to ask how G of the liquid depends on the liquid

configuration or on $h_C(T)$. This can be obtained by studying the temperature dependence of the liquid shear modulus. Previous ultrasonic studies have investigated the pressure dependence of the elastic properties of BMGs, while torsional pendulum experiments have been used to study G [13–15].

Ultrasonic measurements performed at a frequency ω in the megahertz regime measure the “isoconfigurational” (unrelaxed) shear modulus G_∞ for an IS provided that the α -relaxation (slow relaxation) time of the liquid $\tau = \eta(T)/G_\infty$ is much greater than the inverse of the measuring frequency; $\eta(T)$ is the viscosity. As a first step to probing the dependence of G_∞ on the configurational state of the liquid, we measured the longitudinal and transverse sound velocities of $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vit-4) after thermal relaxation to the equilibrium liquid state in a temperature range around T_g . After relaxation, the samples were configurationally quenched to ambient temperature where ultrasonic measurements could be easily performed.

We report results from an ultrasonic study of $G_\infty(T)$. We show that the low-temperature dependence of the elastic moduli is independent of the configuration state. In the equilibrium liquid obtained from the reversible variation of G with annealing temperature, the isothermal relaxation of the shear modulus of the liquid $G_L(T)$ at a given annealing temperature T_A is found to follow stretched exponential behavior, similar to isothermal viscosity relaxation [6]. Cycling between two T_A s results in reversible changes in G showing that the relaxed G is an equilibrium liquid property. For a fixed glass configuration, we find a weakly linear dependence of elastic properties on T as expected from a Debye-Grüneisen (DG) model. Additionally, the implications for the temperature dependence of the liquid viscosity are examined.

Ingots of Vit-4 were prepared by arc-melting a mixture of the elements of purity ranging from 99.5% to 99.999%. These ingots were cast into 8-mm-diameter rods by melting in a stainless steel tube followed by water quenching. The tube and thin reaction layer with the Vit-4 were removed by machining. The amorphicity and homogeneity

of the cast rod were verified through x-ray diffraction and differential scanning calorimetry. The T_g was found to be 627 K with crystallization onset at 727 K. The rod was cut into 3.2-mm-thick slices, which were polished flat and parallel with a surface finish of 2 μm .

The samples were isothermally annealed under argon in sealed quartz tubes in a resistance furnace at a variety of T_A s around T_g and water quenched after each treatment. The total annealing time at each temperature was chosen to be less than the time to the onset of detectable crystallization as determined by the time-temperature transformation for Vit-4 and comparable to the previously determined time for viscosity relaxation to occur [6,16]. This ensured that the samples were in a fully relaxed, glassy state. Provided the rapid water quenching time is short compared to the α -relaxation time at T_A , the relaxed liquid can be configurationally captured; the acoustical properties at room temperature T_{RT} are characteristic of the equilibrium liquid at T_A . The pulse-echo overlap technique with 25 MHz piezoelectric transducers was used to measure the shear and longitudinal wave speeds at T_{RT} for each of the quenched samples [17]. Additionally, from 78 to 298 K, *in situ* sound velocities were measured from samples quenched from $T_A = 567$ and 665 K. Sample density was measured by the Archimedeian technique according to the American Society of Testing Materials standard C 693-93.

To ensure that the quenched samples were truly representative of the equilibrium liquid, the samples were cycled between lower and higher annealing temperatures and the reversibility of the properties was demonstrated. Figure 1 depicts the shear sound velocity C_S relaxation of a sample at 567 K that was initially relaxed and quenched from 652 K. Upon ensuing isothermal annealing at 567 K, this sample shows stretched exponential relaxation towards a unique equilibrium value, following the same form that Busch, Bakke, and Johnson demonstrated for isothermal viscosity relaxation for Vit-4 [6].

$$C_S(t) = C_{S,0} + \Delta C_S [1 - \exp^{-(t/\tau)^\beta}], \quad (2)$$

where $C_S(t)$ is the shear sound velocity at time t , $C_{S,0}$ is the initial C_S , ΔC_S is the total sound velocity change during relaxation into the final equilibrium state $C_{S,eq}$, t is the time in seconds, τ is the characteristic shear flow relaxation time, and β is the stretching exponent. Upon completion of the 567 K relaxation, the same sample was “cycled” back to 652 K, where C_S returned to the same value it had prior to the low-temperature (low- T) annealing. This demonstrates that the measured equilibrium values of the samples annealed and quenched from high T s are representative of the *equilibrium liquid* and have no residual irreversible effects.

Figure 2 shows the temperature dependence of G and the bulk modulus K for equilibrium Vit-4 liquid and *in situ* data from 78 to 298 K on the quenched glass from samples annealed at 567 and 665 K. The glass samples annealed at

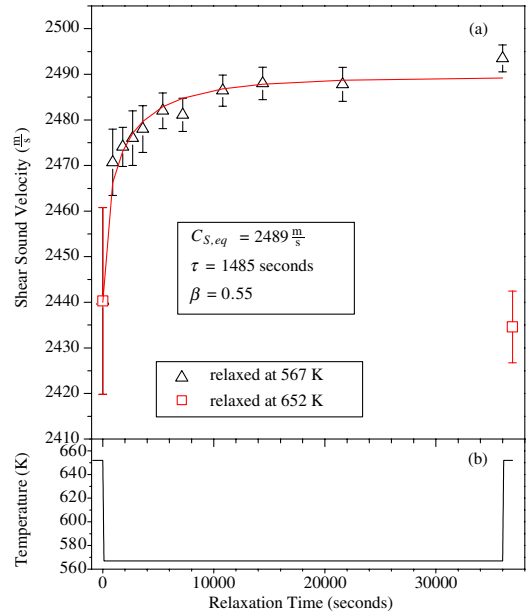


FIG. 1 (color online). (a) Relaxation of Vit-4 C_S at 567 K. Open triangles represent the sample annealed and quenched from 567 K. The fitting parameters are for Eq. (2). After completion of relaxation at 567 K, the sample was annealed at 652 K and the C_S reverted to the value initially measured at 652 K. (b) Temperature profile for the annealing.

different temperatures have different but fixed configurational entropy states, but the linear fits to the low- T modulus data have essentially the same slope, showing that the low- T moduli dependence is independent of the configurational state. This is the expected DG effect of thermal expansion on elastic constants at a fixed glass configuration. The average bulk modulus DG slope was found to be $[dK/dT]_{DG} = -0.006815(\pm 0.0016)$ GPa/K and the average DG shear modulus slope $[dG/dT]_{DG} = -0.009115(\pm 0.00033)$ GPa/K. This thermal expansion effect on the elastic properties was considered when analyzing the T_{RT} data for the samples annealed and quenched from temperatures around T_g . The trend in the moduli measured in the quenched samples at T_{RT} represents the trend that the values should have if they were measured *in situ*. To determine the moduli at the actual annealing temperature, the measured T_{RT} data should be corrected using the DG effect. It is expected that the measured low- T DG dependence of the moduli is a component of the temperature dependence at all temperatures. The data measured at T_{RT} for a sample annealed at T_A should then be corrected by $-(T_A - T_{RT})[dG/dT]_{DG}$ to obtain the actual value of $G(T_A)$. This correction has been included in all of the liquid data shown in Figs. 2 and 3.

At ambient temperature in the “as-cast” sample, G was 35.02 GPa while K was 110.34 GPa; the T_{RT} properties of a fully crystallized sample increased significantly over the glassy material; G increases nearly 26% to 44.21 GPa while K increases 6.5% to 117.5 GPa. In the equilibrium

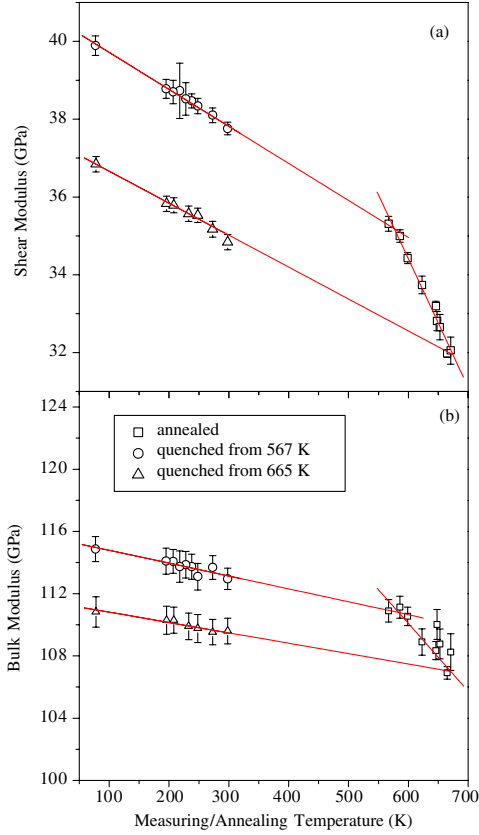


FIG. 2 (color online). (a),(b) The shear and bulk moduli of Vit-4 as measured *in situ* from 78 to 298 K and measured from samples quenched from the equilibrium liquid around T_g . Open circles represent samples annealed at 567 K, open triangles samples annealed at 665 K. Samples annealed at different temperatures, thus having different configuration states, have the same low-temperature slopes. This demonstrates that the low-temperature dependence of the elastic moduli is independent of configuration state.

liquid around T_g , there is a strong linear correlation between both G and K and temperature: $[dG/dT]_L = -0.035$ GPa/K and $[dK/dT]_L = -0.0422$ GPa/K. Although the absolute value of the change of K around T_g is larger than that of G , the relative change in G is much larger. Around T_g , G undergoes relatively greater configurational “softening” than K . G decreases by nearly 9.3% over the 100 K interval from 567 to 671 K, while K only decreases by 2.4% over the same 100 K interval. In summary, the excitation of IS in the liquid leads to a dramatic softening of the shear modulus in the liquid with temperature $G_L(T)$. The T dependence is much greater than the DG thermal expansion effect for a fixed glass configuration $[dG/dT]_{DG}$.

Combining our data for $G_L(T)$ with earlier data for $H_L(T)$ obtained by Busch and Johnson, we can obtain the energy (enthalpy) dependence of G on the configurational enthalpy of the liquid. Specifically, G_∞ of the equilibrium relaxed liquid should be a unique function of P and T or, equivalently, of P and $h_C(T)$. In Busch and Johnson’s

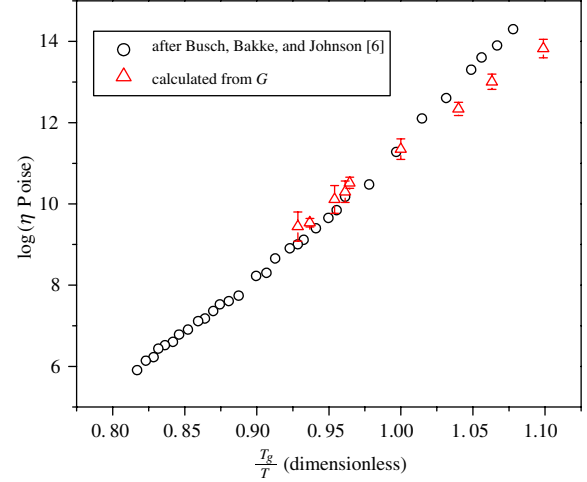


FIG. 3 (color online). Angell plot of the viscosity of Vit-4 as measured by Busch, Bakke, and Johnson [6] (open circles) and calculated from the measured shear modulus following Eq. (5). Above T_g , the viscosities match very well.

paper, $\partial h_C(T)/\partial T$ was found to be 17 J(mol K) $^{-1}$ [9]. Using the definition of enthalpy $h_C(T) = e_C + Pv$ and the fact that the experiments were performed at constant pressure, taking the partial derivative with respect to temperature gives $\partial h_C/\partial T = \partial e_C/\partial T$. Combining $\partial h_C/\partial T$ with the experimental shear modulus data yields that $\partial G/\partial e_C = -2.05$ GPa/(KJ/mol) over the temperature range studied around T_g . This result expresses the dependence of G_∞ on the specific configurational potential energy of the IS of the liquid. This demonstration that $G_L(T)$ falls steeply above T_g suggests that the energy barrier for configurational hopping between IS may be related to $G_L(T)$.

Considering the energy barrier $W(T)$ from Eq. (2) for configurational hopping, one would expect that the liquid viscosity would be of the form:

$$\frac{\eta}{\eta_0} = \exp\left[\frac{W(T)}{k_B T}\right], \quad (3)$$

where η is the viscosity at temperature T , η_0 is the high-temperature limit of the viscosity, k_B is Boltzmann’s constant, and T is the temperature in Kelvin. By using the dimensionless term $y = T_g/T$, Eq. (3) can be recast as:

$$\ln(\eta/\eta_0) = yW(y)/k_B T_g \quad (4)$$

by definition at T_g $\eta = 10^{12}$ Pas and in the high- T (Planck) limit $\eta_0 = 4 \times 10^{-5}$ Pas. Thus, evaluating Eq. (4) at T_g yields 37.8, a value that should be nearly constant for all glasses. Angell defined liquid fragility as [7]:

$$\begin{aligned} m &= \left[\frac{d \log(\eta(y))}{dy} \right]_{y=1} \\ &= \frac{W(1)}{2.303 k_B T_g} \left[1 + \left[\frac{d \ln W(y)}{dy} \right]_{y=1} \right] = 16.4[1 + i], \end{aligned} \quad (5)$$

where i is a reduced liquid fragility index related to the logarithmic derivative of $W(y)$ evaluated at T_g . According to Eq. (1), the temperature dependence of $W(y)$ should include $G(T)$ or $G(y)$. Following Johnson and Samwer, we assume γ_{C0} to be independent of y . Thus, only the CSZ effective volume $\Omega_{\text{eff}}(y) = \Omega\zeta$ has a possible temperature dependence; allowing for this, Eq. (5) becomes $m = 16.4[1 + i] = 16.4[1 + n + p]$, where n and p are reduced “elastic fragility” and “CSZ volume fragility” indices:

$$\begin{aligned} n &= [d\ln(G(y))/dy]_{y=1} \\ &= -(T_g/G(T_g))[dG(T)/dT]_{T_g} \\ \text{and } p &= [d\ln(\Omega_{\text{eff}}(y))/dy]_{y=1} \\ &= -(T_g/\Omega_{\text{eff}}(T_g))[d\Omega_{\text{eff}}(T)/dT]_{T_g}. \end{aligned} \quad (6)$$

Figure 3 is an Angell plot depicting the Newtonian viscosity for Vit-4 calculated from the shear modulus as outlined above and measured by parallel plate rheometry and three-point beam bending [6]. The measured viscosity yields an Angell fragility parameter of $m = 33(\pm 1.5)$ and fragility index $i = 1.0$. Later data of Masuhr that includes high- T Couette viscometry measurements yields $m \sim 37$ or $i \approx 1.3$ [18]. Applying Eq. (6) to the present data for $G_L(T)$, we obtain $n = 0.65$ and an Angell fragility of $m = 28.6(\pm 1.1)$. Comparing the reduced fragility indices calculated from the measured G with those from viscosity measurements, there is a discrepancy between i and n of 0.35–0.65. Thus, the steep temperature dependence of $G_L(T)$ found in this study does not account solely for the entire reduced fragility index of Vit-4; perhaps the difference should be attributed to the temperature dependence of the effective volume. From PEL studies, one expects as temperature is increased the characteristic CSZ barrier crossing events will involve atomic clusters of decreasing volume and, thus, decreasing cooperativity [19]. The present data suggest that a power law behavior of the form y^p , with $p \sim 0.35$ –0.65, may provide an apt description of this dependence in Vit-4; however, the exact functional form above $1.2T_g$ has yet to be experimentally measured. This model relating viscosity to shear modulus is similar to the “shoving” model put forth by Dyre, Olsen, and Christensen; the main difference between them is in the details of the functional form taken for the energy barrier to configurational hopping or a flow event [20].

In conclusion, in the limited temperature range around T_g that was studied, the temperature dependence of the liquid shear modulus G_L for Vit-4 was found to be linear and much stronger than that of the bulk modulus K . The temperature dependence of G_L in the liquid state is much steeper than the DG dependence of the configurationally frozen glass. The dramatic change in the slope of G from glass to liquid corresponds to a strong dependence of G on the configurational potential energy of the liquid. This finding provides support for the idea that the barrier height for configurational change in the liquid PEL scales with

shear modulus. Using a simple model, we compared the rheological fragility measured for Vitreloy 4 with that predicted from the temperature dependence of the shear modulus utilizing the CSZ model of Johnson and Samwer. The experimentally determined slope of $G_L(T)$ and corresponding elastic fragility index $n = 0.65$ accounts for most, but not all, of the liquid fragility index $i = 1.0$ –1.3. This suggests that the remaining part of i arises from the decrease in *size* of CSZ’s with increasing temperature. To explain our data, a “volume fragility index” of $p \sim 0.35$ –0.65 is required.

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