Volume Expansion Measurements in Metallic Liquids and Their Relation to Fragility and Glass Forming Ability: An Energy Landscape Interpretation

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Recent studies of Cu-Zr glasses have reported a rapid variation in the amorphous phase density near the optimal glass forming compositions, supporting the belief that the densest liquids are also the best glass formers. Here, we show that the measured densities of the Cu-Zr liquids at higher temperatures are not peaked sharply near these compositions, but the volume expansivities are. Theoretical studies have shown that the expansivity correlates with fragility near T_g; the experimental results presented here show that at high temperature they become anticorrelated. From energy landscape arguments, this indicates the existence of a crossover temperature for the expansivity-fragility correlation that scales inversely with the liquid fragility. These results lead to an improved understanding of the high temperature properties of liquids that form glasses and suggest a new method for identifying the best glass forming compositions within an alloy system from the properties of the equilibrium liquids.

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For many years following their discovery [1], the production of metallic glasses required rapid cooling or quenching of the liquids (10^5 to 10^6 K/s) [1,2], significantly limiting their usefulness. Following earlier work [3], a new class of metallic glasses became available, which could be prepared at slower cooling rates comparable to those used for the silicate glasses [2,4]. Because of their ease of production and desirable physical properties, these glasses are increasingly finding technological applications [5,6]. However, why some metallic liquids easily form glasses, while others do not, is a key unresolved question.

It is widely believed that the density of the liquid is linked to glass formability, since high-density liquids are taken to be thermodynamically more stable and to have a higher viscosity. Recently reported measurements of the relative densities of a series of $Cu_{100-x}Zr_x (30 \leq x \leq 54)$ glasses show this correlation [7]. The smallest density changes on crystallization, suggesting a more dense amorphous phase, were observed for $Cu_{50}Zr_{50}$, $Cu_{56}Zr_{44}$, and $Cu_{64}Zr_{36}$ [7], which are precisely the best glass forming compositions, as determined from the maximum dimensions that can be cast into the amorphous state (critical thickness) [7–13]. Here, we present the corresponding liquid data for the density and the volume expansion coefficient for 38 compositions of Cu-Zr. To within measurement error, no local density maxima were observed in equilibrium or supercooled liquids; instead, maxima in the thermal expansion coefficient were observed. This indicates that the structural evolution that leads to the higher density in the glasses must occur in liquids at intermediate temperatures, likely on approaching the glass transition temperature, T_g.

In addition to identifying a new method for finding the best glass forming compositions from properties of their liquids, these results shed new light on the relation between the fragility classification (*strong or fragile*) for liquids [14] and their expansion coefficients at high temperatures. Liquids are *strong* when the temperature dependence of the response functions (viscosity, diffusivity, relaxation time, excess entropy of the liquid over that of the crystal, etc.) is Arrhenius over a wide temperature range. They are successively more *fragile* as these quantities show more non-Arrhenius (Vogel-Fulcher-Tammann, stretched exponential, etc.) behavior. While there are some exceptions (e.g., Sorbitol, Salol), strong liquids, such as SiO_2, tend to be better glass formers than very fragile liquids; for metallic glasses, we are not aware of any exception to this trend [15–18]. In agreement with this trend, the density data for the Cu-Zr glasses [7], molecular dynamics (MD) simulations of the liquid viscosity [19], and diffusion coefficients [20], as well as viscous flow measurements near the glass transition [21], indicate that the best Cu-Zr glasses and their liquids are stronger.

Since theoretical studies have shown that the volume expansion coefficient also correlates with fragility, a larger expansivity near T_g signals a more fragile liquid [22,23]. It would, therefore, be expected that the best glass forming liquids will have a smaller thermal expansion coefficient, in addition to having a larger density and being stronger. The data presented here show that the reverse is true at higher temperatures, with stronger liquids having the larger expansion coefficient. As will be discussed, this is in agreement with energy landscape arguments, which suggest a crossover behavior (e.g., the expansivity of stronger glasses becoming larger than that of fragile glasses in the liquid state) at higher temperatures. For Cu-Zr, the data presented here show that this crossover temperature occurs between the T_g and $2T_g$.

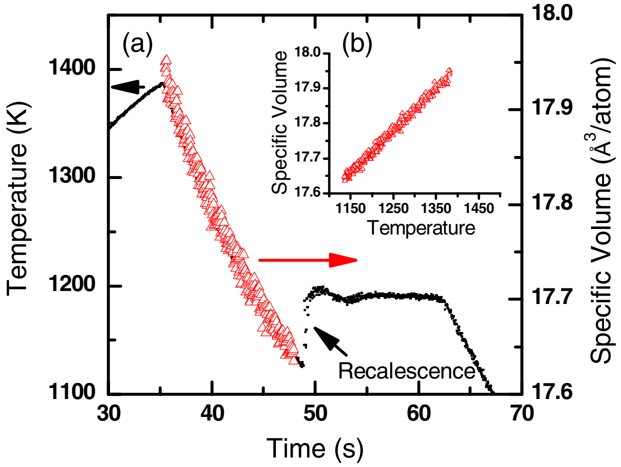

FIG. 1 (color online). (a) Temperature (■) and specific volume (△) as a function of time for a $Zr_{46}Cu_{54}$ liquid during a representative radiative cooling cycle. The abrupt temperature rise near 48 s is due to crystallization (recalescence). (b) Specific volume versus temperature curve during this cycle.

Samples of $Cu_{100-x}Zr_x (30 \leq x \leq 54)$ were levitated in high vacuum ($\sim 10^{-7}$ torr) in an electrostatic levitation facility and were melted using a 50 W diode laser. The volumes of the liquids were determined as a function of temperature from the video images of the two-dimensional (2D) silhouette. The volume was computed by integrating the 2D image around an axis of symmetry (see Refs. [24–28] and the Supplemental Material [29] for more details).

Average volume as a function of temperature was obtained from multiple radiative cooling studies at each sample composition. A representative data set is shown in Fig. 1(a), and the specific volume (average volume per atom) calculated from the measured volume as a function of temperature is shown in Fig. 1(b). The coefficient of thermal expansion [$\beta = (\partial \ln V/\partial T)_P$] was determined from linear fits to the volume-temperature data. The error in the absolute volume is dominated by the uncertainty in the volume and mass calibrations (± 0.5% tolerance). These uncertainties cancel in the thermal expansion calculations. There, the dominant contributions to the error are the uncertainty in the temperature calibration (± 1% tolerance) and the uncertainty in the linear fit to the data ($\approx \pm 1\%$ to 95% confidence), giving a total uncertainty in β of $\approx \pm 2\%$.

The specific volume and thermal expansion coefficients of 38 Cu-Zr liquid compositions were measured over approximately 200 K above and 50 K below their liquidus temperatures, T_l. Since the relevant temperature for glass formation is T_g, for a meaningful comparison among all alloy compositions, the data are shown in Fig. 2 at a normalized temperature of $2T_g$. T_g was estimated from a linear fit to the published data [30], using the relation T_g (K) $= 866.48 - 3.91x$, where x is the atomic percent of Zr. The specific volume shows an approximately linear increase with increasing Zr, as would be expected from a rule of mixtures argument for an ideal system. The statistical error in the measured volume of the liquids limits the detection of a density fluctuation to within about 1%, which is approximately 3/4 of the magnitude of the largest peak reported in the glass density [7]. Within this error, no peaks are evident in the liquid density as a function of composition. In contrast with the volume data, however, statistically significant local maxima are observed in the thermal expansion.

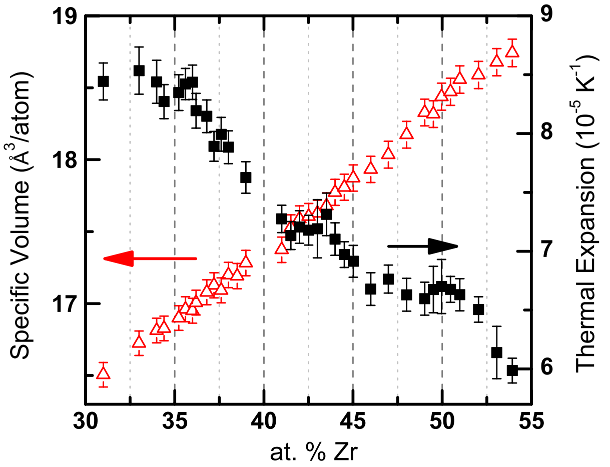

FIG. 2 (color online). Specific volume (△) and thermal expansion coefficient (■) of liquid $Cu_{100-x}Zr_x$ at twice their respective glass transition temperatures, T_g (i.e., $2T_g$).

To show the local maxima more distinctly, the normalized expansivity, β_N, are plotted in Fig. 3,

$$\beta_N = (\beta_{\text{Exp}} - \beta_{\text{Cal}})/\beta_{\text{Cal}}, \tag{1}$$

where β_{Cal} is the expected expansivity that follows the approximately linear trend with Zr concentration,

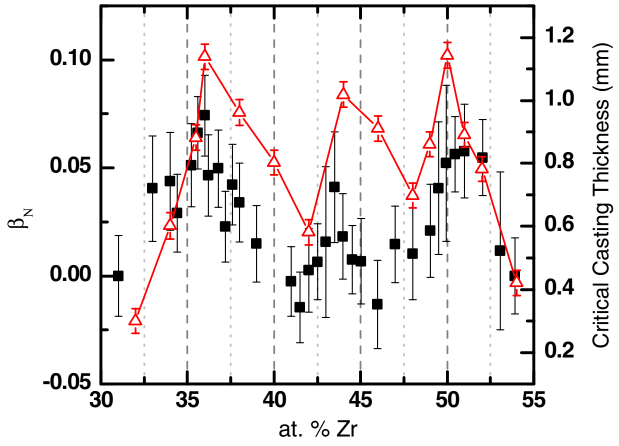

FIG. 3 (color online). Normalized liquid thermal expansion from the present measurements (■) and critical casting thickness (△, taken from Ref. [7]) of Cu-Zr liquids.

calculated by assuming an ideal rule of mixtures based on the β_{Exp} values for the highest and lowest Zr concentrations studied. Clearly defined peaks in β_N are observed at 50.5, 43.5, and 36 at. % Zr (Fig. 3), which are the compositions of maximum critical thickness (best glass formation) determined previously [7–13]. Although the data reported here are measured at $2T_g$, within a given composition dV/dT was constant across the entire 250 K range.

Some correlations between volumetric properties and glass forming ability (GFA) in metal alloys have been suggested previously [31–37]. However, the reported correlations between expansivity and GFA are inconsistent and sometimes contradictory [35,37]. It is crucial to note that these correlations are deduced from studies of liquids containing different elements, with different baselines and different anharmonicities. In contrast, the results presented here were obtained by systematically changing composition within the *same* alloy system, yielding the first clean correlation between liquid thermal expansion and GFA.

As noted previously, near T_g a large thermal expansion in the liquid is correlated with a high fragility, and hence anticorrelated with GFA. To understand why this correlation found near T_g conflicts with the one reported here for high temperature, it is necessary to see how properties evolve over the ~500 K between the liquidus and glass transition temperatures. The definitions of strength and fragility in the Angell scheme [14] and within the context of the energy landscape formalism [38] are also needed.

The *strong or fragile* definition in terms of the atomic mobility and thermodynamic properties has already been mentioned. The energy landscape provides a statistical mechanical way of understanding the origin of this behavior in terms of structure. The landscape is the potential energy surface formed by the $3N$ atomic coordinates in a $3N + 1$ dimensional space. Within this formalism, atomic structures (configurations with qualitatively similar pair distribution functions) are found within low energy portions (basins) of the energy landscape [38]. The fragile-or-strong classification refers to the temperature dependence of the energy landscape sampling. Liquids that continue to favor the atomic structures associated with the glass to higher temperatures are defined as strong, while liquids whose probability distributions rapidly "smear out" over the energy landscape with increased temperature are defined as fragile [14]. These considerations define three distinct temperature regimes for liquids: (i) a low temperature region where basin occupancy is fixed and changes in the average structure are dominated by vibrational effects; (ii) a high temperature region where the entire energy landscape is sampled so that changes in the aggregate structure are dominated by Boltzmann statistics; and (iii) a transitional temperature range where neither are dominant. These correspond to the landscape dominated flow, free diffusion of atoms, and the landscape-influenced flow, as identified by Debenedetti and Stillinger [39].

The absence of density maxima in the equilibrium liquids suggests that near the liquidus temperature the Cu-Zr system is approaching the highly fluid temperature regime corresponding to a "smeared out" average structure [39]. The peaks in thermal expansion show that the better glass forming liquids approach their high-density glassy state more rapidly with cooling (as expected for stronger liquids) than do liquids of nearby compositions.

Based on these considerations, the relationship between thermal expansion and fragility then depends on the temperature region in which the thermal expansion coefficient is measured. As noted by Stillinger and Debenedetti, in liquids and glasses the temperature dependence of the volume expansivity can be separated into two parts: (i) "vibrational changes," within a configurational basin, and (ii) "structural changes," i.e., changes in the probability distribution among the basins. In the landscape dominated region, the temperature dependence of the expansivity in the amorphous solid is determined only by the vibrational contribution [22]. As for crystal solids, this is governed by the anharmonicity of the atomic potential. Upon heating to just above T_g, the vibrational properties of the glass remain manifest in the supercooled liquid [23,40]. Additional contributions from rapid structural changes in the liquid increase the expansion coefficient. Therefore, a fragile glass shows a higher thermal expansion coefficient in the supercooled liquid just above T_g than a stronger glass [22,41]. In contrast, in the free diffusion high temperature range, the landscape becomes of marginal importance, blurring the meaning of a fragility distinction.

It is less clear what happens at intermediate temperatures, in the landscape-influenced regime. While the expansion coefficient for a fragile liquid is larger near T_g, the Cu-Zr data presented here show that it is smaller in the landscape-influenced regime, indicating that a crossover occurs. All of the Cu-Zr liquids are fragile; those compositions associated with the maxima in expansivity are just less fragile (hereafter referred to as stronger to avoid confusion). To understand the results presented here, then, it is useful to examine how the energy landscape (depth and degeneracy of the basins) changes for such liquids of similar composition but slightly different fragilities. As illustrated in Fig. 4(a), the stronger liquids have a larger number of low energy glasslike configurations than do the more fragile liquids, making them thermodynamically more stable. This stability is reflected by the wider temperature range over which the stronger liquids have smaller fractions of excited states [Fig. 4(b)], corresponding to a smaller number of configurations and a wider landscape-influenced region. In Fig. 4(c), this is reflected in the more gradual increase in shear viscosity on approaching T_g for a stronger liquid, versus the sharper rise in viscosity near T_g in the more fragile liquid (shown in an Angell plot).

Since the probability distribution among basins changes most in the landscape-influenced region, properties of the

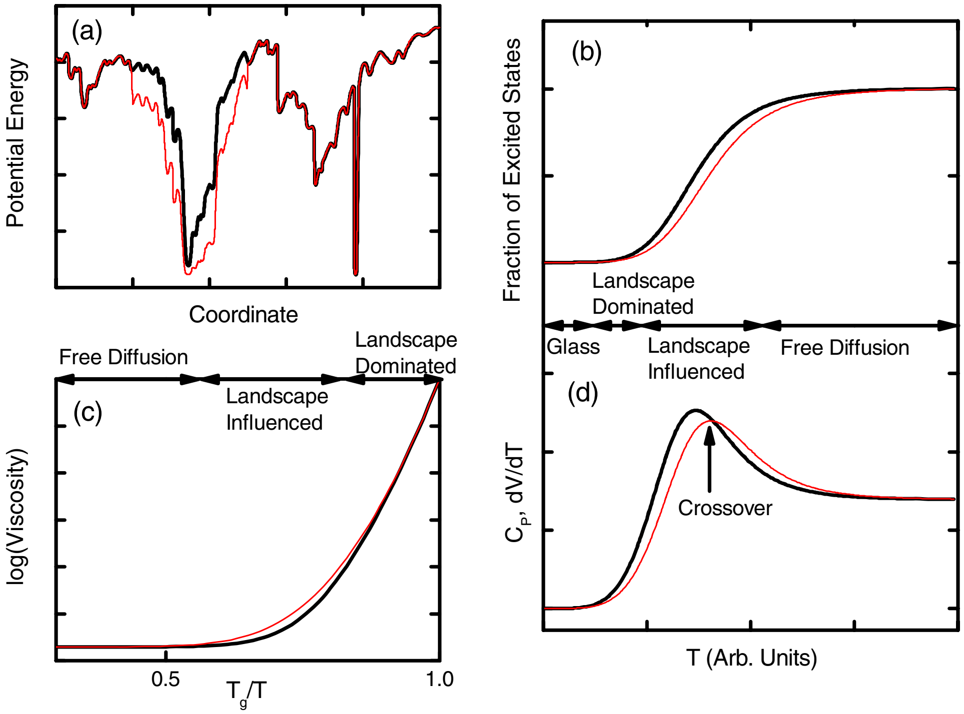

FIG. 4 (color online). Interpretation of the distinction between "fragile" (thick black lines) and "stronger" (less fragile, thin red lines) liquids of similar composition in terms of (a) the topology of the energy landscape (adapted from Refs. [14,39]), (b) the temperature (T) dependence of the fraction of thermally excited configurations (adapted from Ref. [14]), (c) the Arrhenius representation of liquid viscosity (Angell plot), and (d) second derivatives of Gibbs free energy (i.e., specific heat and thermal expansion). A crossover is evident at an intermediate temperature.

liquid that are configuration-dependent, such as enthalpy and volume, will also undergo large changes. The derivatives of these quantities, i.e., specific heat and thermal expansion, have a maximum within this region, followed by a crossover at higher temperatures when liquids with different fragilities are compared [Fig. 4(d)]. The sudden increase and a maximum just above T_g are common features of all liquids, where the rise correlates with fragility [42]. However, how these properties evolve in supercooled metallic liquids of different fragilities is not known from experimental data because of rapid crystallization. Interestingly, data for glycerol (a fragile liquid) [43] are consistent with these energy landscape arguments. The experimental results reported here, along with the viscosity data at high temperatures [44], then indicate that the Cu-Zr liquids must be on the high temperature side of the landscape-influenced regime at $2T_g$.

A simpler qualitative explanation can be given in terms of entropy and volume fluctuations [45] in the supercooled liquid above T_g. The volume expansion coefficient is proportional to the cross fluctuation terms in volume and entropy, $\langle \delta V \delta S \rangle$, corresponding to an infinitesimal change in temperature, δT. The excess entropy and volume of a fragile liquid over that of the corresponding crystal phase increase much more rapidly above and near T_g, compared to a strong liquid [46]. Therefore, the expansion coefficient of a fragile liquid is expected to be large just above T_g. Thereafter, it should decrease more rapidly with increasing temperature than for a stronger liquid. This naturally leads to a crossover temperature, above which the fragile liquid will have a smaller expansion coefficient than a stronger liquid, in agreement with the energy landscape argument and the experimental observation. Consistent with evidence from other studies, then, stronger liquids are the best glass formers in Cu-Zr. Those liquids will have a *larger* thermal expansion coefficient at high temperatures, which is opposite to what might be expected based on considerations made near the glass transition temperature, below the crossover temperature.

To our knowledge, this is the first comparative study of changes in the thermal expansivity as a function of composition and what they reveal about fragility in supercooled and equilibrium liquids within the same chemical system. By confining the studies to the same chemical system, obfuscations from differences in chemical bonding and anharmonic contributions to the potential, which can dominate the behavior of the expansivity, are avoided. As a result, a cleaner correlation between the thermal expansion of the liquid at high temperature and glass formability has been established. The narrow composition range over which peaks in the expansivity are present indicates that the structural features that lead to better glass formation are strongly composition dependent. The experimental results presented here suggest that an extension of modeling efforts to focus on correlations between physical properties (such as the expansivity) and the kinetic and thermodynamic fragility of the high temperature liquids will lead to new predictive methods for glass formation and a deeper understanding of the meaning of liquid fragility.

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