Anomalous system-size dependence of properties at the fragile-to-strong transition in a bulk-metallic-glass forming melt

Sergey V. Sukhomlinov*, Martin H. Müser

Dept. of Materials Science and Engineering, Universität des Saarlandes, 66123 Saarbrücken, Germany

ABSTRACT

As many other glass formers do, bulk-metallic-glass (BMG) forming melts undergo a fragile-to-strong transition (FST), which is accompanied by a small but noticeable peak in the specific heat c_p. Because of this peak, the FST is sometimes interpreted as a smeared-out phase transformation. Finite-size scaling analysis of peaks in c_p allows the order of a phase transition to be accurately determined. This motivated us to study c_p along with structural and dynamical properties of a ternary BMG former ($Zr_{0.606}Cu_{0.29}Al_{0.104}$) using computer simulations, in which the system size was varied in a well-controlled fashion. Our model system reproduces the typical, almost discontinuous cross-over between non-Arrhenius to Arrhenius-type dynamics, which defines the FST. However, in contrast to the expectations for a phase transformation, the larger the system the smaller the peak in c_p. Other properties also reveal a size dependence, which is difficult to reconcile with the interpretation of the FST being a (smeared-out) phase transformation resulting from the competition between different local structures.

1. Introduction

A feature of many glass formers is the existence of a transition temperature, at which the temperature-dependent shear viscosity $\eta(T)$ and other dynamical properties cross over from a high-temperature, non-Arrhenius dependence to a low-temperature Arrhenius-type dependence [1–11]. Thus, relaxation times and viscosities are proportional to $\exp(-\Delta E/k_B T)$ with a constant (apparent) energy activation barrier at small temperatures T for so-called "strong" liquids, where ΔE may still depend on the property and pressure but not on T. In contrast, in the high-temperature, "fragile" liquid, ΔE generally increases noticeably with decreasing temperature, potentially because of entropic effects [12]. At the same time, the specific heat c_p of fragile liquids tends to exceed $3k_B$ per atom – the value for any classical, harmonic solid – by more than 50%, while strong liquids surpass it only by 15% or less [13]. Thus, the fragile liquid changes its structure much more substantially with T than the strong liquid, which can be the reason for a cross-over in the dynamic behavior [13].

The fragile-to-strong transition is an omnipresent phenomenon not only in BMG formers [8,9,14,15] but also in other classes of glass-forming systems, for example, in tetrahedral network liquids including traditional silicate melts [7,16–22]. FST-like phenomena have even been observed outside thermal equilibrium, most notably in metastable, supercooled water [23–31].

Multiple experimental [32,33] and theoretical [7,18,34] works have attempted to unravel the nature of FSTs. In loose analogy to phase transformations in crystalline solids, it was proposed that the competition between different local structures could be at the root of FSTs. In the simplest case, two competing local structures may have a noticeable density difference [18,23,27,35–37]. Generally, the precise nature of the structural differences between possible competing phases has so far remained rather vague in the context of FSTs. Despite few attempts [34], the concept of well-defined order parameters has not yet been put forth to FSTs as successfully or as rigorously as for phase transformations involving symmetry breaking [38]. Yet, the idea of competing phases differing in structure has been proposed to apply to the FST in BMG-forming melts [39] as well. It was even argued that the FST in network glass formers [40] as well as in BMG-forming melts [32] could be associated with an underlying lambda transition, which is continuous (i.e., second order) rather than discontinuous (i.e, first order). The perhaps most-promising theory to describe the dynamical anomalies that occur at the FST is the mode-coupling theory (MCT) [7,41,42], which is not considered here, because it does not explain the existence of anomalies in thermal or structural properties at the FST.

All of the above scenarios, except for MCT, imply that the FST in liquids is thermodynamic in nature, or, that it has at least a thermodynamic aspect akin of phase transitions, as they occur, for example in crystals. If this were true, the FST should be expected to become sharper with increasing system size [38,43]. The reason for this claim is that thermal fluctuations make small systems "peek" much more frequently from the more stable phase into the less stable phase than large systems. This is because the free-energy barriers to convert between the two phases as well as their free-energy differences decrease with decreasing system size. In fact, a transition can only be said to occur rigorously in

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* Corresponding author.

E-mail address: sergey.sukhomlinov@uni-saarland.de (S.V. Sukhomlinov).

the thermodynamic limit of infinite particle numbers $N \to \infty$.

There have been surprisingly few, perhaps even no studies systematically addressing the question how system size affects the FST of a given glass-forming melt. In this work, we attempt to close this gap by running molecular-dynamics (MD) simulations of an appropriate model system. Originally, we meant to mimic the alloy $Zr_{0.585}Cu_{0.156}Ni_{0.128}Al_{0.103}Nb_{0.028}$, because it exhibits a rather pronounced peak in c_p near the FST [33]. However, due to the lack of reliable potentials for Ni and Nb in this alloy, we replaced Ni and Nb atoms isoelectronically with Cu and Al atoms, resulting in the composition $Zr_{0.606}Cu_{0.29}Al_{0.104}$. While this substitution – or perhaps the imprecision of the employed potentials – lead to a noticeable suppression of the peak, all mentioned, generic features that commonly occur at FSTs remained intact. Moreover, density, transition temperature, structure factors, etc. turned out close to the experimental reference alloy, which is why we feel confident that the simulation results are robust. Last but not least, our simulations reveal how $Zr_{0.606}Cu_{0.29}Al_{0.104}$ would behave if interactions were slightly different than they are in reality. A general understanding of the FST should certainly apply to such an alloy as well.

The remainder of this paper is organized as follows: Model and methods are sketched in Section 2. Section 3 contains the results and some discussion. Conclusions are drawn in Section 4.

2. Model and methods

We model the alloy $Zr_{0.606}Cu_{0.29}Al_{0.104}$ with an embedded-atom potential, which was specifically designed for Zr-Cu-Al ternaries and convincingly tested [44]. Simulations are run in the NpT ensemble using LAMMPS [45] with system sizes ranging from $N = 96$ to $N = 8788$. Pressure is controlled with a Nosé-Hoover chain [46] and temperature with a Langevin thermostat [47].

In order to speed up the dynamics of the Zr and Cu subsystems in the ternary alloy, the masses of both Zr and Cu were replaced with that of the lightest atom in the system, i.e., Al. The substitution only affects the vibrational and attempt frequencies but leaves structural, thermodynamic, and even energy barriers in the configurational space unchanged. This is because the Boltzmann factor of a classical system factorizes into a kinetic and a configurational contribution. Thus, prefactors of relaxation times and viscosities are slightly reduced, however, their temperature dependence remains unaffected.

The specific heat, which is a central observable in this work, is calculated in two different ways: (i) from the enthalpy fluctuations at a given temperature and (ii) from taking the numerical derivative of the enthalpy $H(T)$ through finite differences. The two methods give similar results when equilibration and observation times clearly exceed the intrinsic relaxation time, but quickly deviate from one another otherwise. In this work, we only report the specific heat down to those temperatures, where both methods give similar results.

Note that unlike Monte Carlo (MC), MD suffers from (small) timestep discretization errors. This leads to minor systematic errors in the computation of c_p, which furthermore slightly differ between the two employed methods. We therefore ensured that the errors in c_p remain below $0.015 k_B$ per atom, which corresponds to 1% of the configurational specific heat of a harmonic solid. The reason why we preferred MD over MC is that MC produces intrinsically overdamped dynamics and that MD samples phase space more efficiently than MC, at least as long as the MC trial moves consist only of local moves.

3. Results and discussion

3.1. Dynamical properties: volume and energy relaxation time

A systematic study of BMG-forming melts revealed that the transition between a fragile and a strong liquid is a general feature of these alloys [9]. It is also widespread in other classes of glass-forming melts

[1–3,7,11]. The cross-over from a non-Arrhenius to an Arrhenius-type dependence at the FST is seen for different dynamic properties at the same temperature. However, the apparent activation barrier $\Delta E \equiv \partial \ln \tau / \partial \beta$ may depend on the property τ, which can be, for example, the volume relaxation time (defined further below) or the shear viscosity η. While experimentalists often measure the shear viscosity, its computation is numerically demanding, because the respective estimators require "expensive" second-order derivatives of the potential energy to be taken and statistics are tedious to acquire.

Since our simulations are run in the NpT-ensemble, we measure the volume autocorrelation function (ACF) instead. It is defined here as

$$C_{VV}(t) \equiv 1 - \frac{\langle \{V(t+t') - V(t')\}^2 \rangle}{\langle \delta V^2 \rangle}, \tag{1}$$

where $V(t')$ is the volume at time t'. In Eq. (1), $\langle \ldots \rangle$ indicates a time average in thermal equilibrium and $\langle \delta V^2 \rangle$ the variance of the volume. The ACF is defined such that $C_{VV}(\infty) = 0$ and $C_{VV}(0) = 1$. This allows a mean volume correlation time to be defined as

$$\tau_V \equiv \int_0^\infty C_{VV}(t) dt. \tag{2}$$

This correlation time can also be associated with a relaxation time, because for a small temperature or pressure change inducing a small change ΔV in the mean volume, we observe that the relaxation obeys

$$\langle V(t) - V(0) \rangle = C_{VV}(t) \cdot \Delta V, \tag{3}$$

once t has exceeded a few inverse Debye frequencies. This time, $\langle \ldots \rangle$ denotes a disorder average over different random realizations. Since the integral is dominated by large times, the minor differences between volume ACF and volume relaxation function are not significant.

To make the integration in Eq. (2) numerically stable at large times, we fit $C_{VV}(t)$ with a purely empiric, analytic function and performed the integration over the fit function rather than over the original data. We found

$$C_{VV}(t) = a \exp\{-(t/\tau_s)^\beta\} + b \ln \frac{t_2^2 + t^2}{t_1^2 + t^2}. \tag{4}$$

to describe the volume ACF rather well, i.e., more accurately with the same number of parameters than commonly used relaxation functions, such as two superimposed stretched exponentials. In Eq. (4), a, τ_s, β, b, t_1 and t_2 are fit parameters. Examples of such fits are shown in the inset of Fig. 1.

The main panel of Fig. 1 reveals that the apparent activation barrier
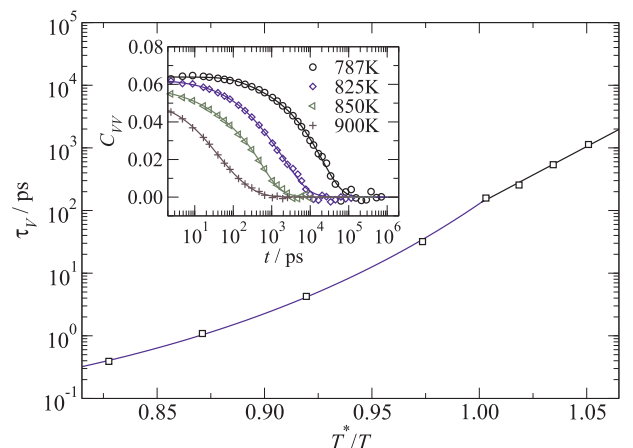
Fig. 1. Main figure: Volume relaxation times τ_V as a function of reduced inverse temperature T^*/T. The FST temperature T^* is estimated to be $T^* = 830$ K. The apparent activation energy for the volume relaxation is $\Delta E_V = 3.2$ eV, which is proportional to the slope of the black line. The $\tau_V(T)$ curve was fitted using Eq. (5). Inset: Simulation data on the volume ACF at selected temperatures including fits of the $N = 8788$ data to Eq. (4), from which τ_V was deduced.