

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

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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 ($\text{Zr}_{0.606}\text{Cu}_{0.29}\text{Al}_{0.104}$) 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 expectation for any 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 local structures.

I. 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 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. 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 [12].

The fragile-to-strong transition is an omnipresent phenomenon not only in BMG formers [8, 9, 13, 14] but also in other classes of glass-forming systems, for example, in tetrahedral network liquids including traditional silicate melts [7, 15–21]. FST-like phenomena have even been observed outside thermal equilibrium, most notably in metastable, supercooled water [22–30].

Multiple experimental [31, 32] and theoretical [7, 17, 33] 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 [17, 22, 26, 34–36]. 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 at-

tempts [33], 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 [37]. Yet, the idea of competing phases differing in structure has been proposed to apply to the FST in BMG-forming melts [38] as well. It was even argued that the FST in network glass formers [39] as well as in BMG-forming melts [31] 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, 40, 41], 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 [37, 42]. 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 the thermodynamic limit of infinite particle numbers $N \rightarrow \infty$.

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 $\text{Zr}_{0.585}\text{Cu}_{0.156}\text{Ni}_{0.128}\text{Al}_{0.103}\text{Nb}_{0.028}$, because it exhibits a rather pronounced peak in c_p near the FST [32]. However, due to the lack of reliable potentials for Ni and Nb in this alloy, we replaced Ni and Nb atoms isoelectroni-

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cally with Cu and Al atoms, resulting in the composition $\text{Zr}_{0.606}\text{Cu}_{0.29}\text{Al}_{0.104}$. 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 $\text{Zr}_{0.606}\text{Cu}_{0.29}\text{Al}_{0.104}$ 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 Sect. II. Sect. III contains the results and some discussion. Conclusions are drawn in Sect. IV.

II. MODEL AND METHODS

We model the alloy $\text{Zr}_{0.606}\text{Cu}_{0.29}\text{Al}_{0.104}$ with an embedded-atom potential, which was specifically designed for Zr-Cu-Al ternaries and convincingly tested [43]. Simulations are run in the NpT ensemble using LAMMPS [44] with system sizes ranging from $N = 96$ to $N = 8788$. Pressure is controlled with a Nosé-Hoover chain [45] and temperature with a Langevin thermostat [46].

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. This substitution only affects the vibrational and attempt frequencies but leaves energy barriers in the configurational space unchanged. 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) time-step 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 as long as the trial moves in

MC consist only of local moves.

III. RESULTS AND DISCUSSION

A. 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] – and 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

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

where $V(t')$ is the volume at time t' . In Eq. (1), $\langle \dots \rangle$ 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

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

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

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

once t has exceeded a few inverse Debye frequencies. This time, $\langle \dots \rangle$ 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

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

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.

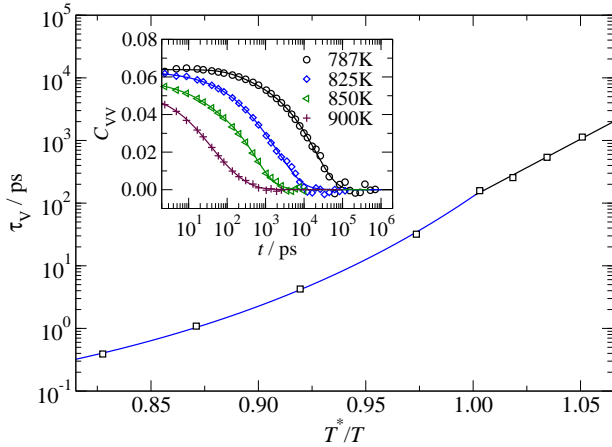


FIG. 1. Main figure: Volume relaxation times τ_V as a function of reduced inverse temperature T^*/T . The FST temperature T^* is estimated to be $T^* = 830$ K. The apparent activation energy for the volume relaxation is $\Delta E_V = 3.2$ eV, which is proportional to the slope of the black line. The $\tau_V(T)$ 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.

The main panel of Fig. 1 reveals that the apparent activation barrier ΔE_V is slightly dependent on T for $T > T^*$ but apparently independent of T for $T < T^*$. Moreover, ΔE_V is (quasi-) discontinuous at T^* , i.e., it is smaller for the strong than for the fragile liquid. These observations are consistent with simulation data on self-diffusion coefficients in BMG-forming melts [10] and with experimental data on shear viscosities of glass-forming colloids [11]. To describe the dependence of relaxation times on temperature, we adopted the commonly used expression for the shear viscosity [47], which is referred to as Mauro-Yue-Ellison-Gupta-Allan (MYEGA) equation. This relation was derived from the Adams-Gibbs equation through a model for the configurational entropy. In contrast to a simple, i.e., linear Taylor series expansion of ΔE , which would have been sufficient here, the MYEGA equation has well-behaved properties in the limit of large temperatures and does not diverge at any finite temperature. This was our motivation for its use. Here we adopt the relation to relaxation times according to

$$\ln(\tau_V/\tau_V^\infty) = \frac{BT^*}{T} \exp\left(\frac{CT^*}{T}\right), \quad (5)$$

where τ_V^∞ , B and C are empiric fit parameters. Fits of the modified MYEGA equation to our simulations data on volume relaxation times are shown on the main panel of Fig. 1.

The analysis of the ACF and the deduced relaxation times was repeated for the energy. Any function and observable was defined as above. For the precise definition, the letter V for “volume” only needs to be replaced with “E” for energy. Results are summarized in Fig. 2. We note that only the potential energy was included in the energy ACF, since the response of the kinetic energy is quasi instantaneous and unrelated to the structural relaxation.

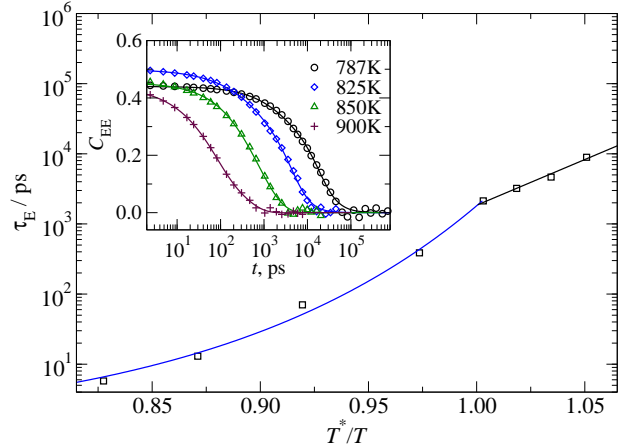


FIG. 2. Main figure: Energy relaxation time τ_E as a function of reduced inverse temperature T^*/T . The FST temperature T^* is estimated to be $T^* = 830$ K. The apparent activation energy for the energy relaxation is $\Delta E_E = 2.3$ eV, which is proportional to the slope of the black line. The $\tau_E(T)$ curve was fitted using Eq. (5). Inset: Simulation data on the energy ACF at selected temperatures including fits of the $N = 8788$ data to Eq. (4), from which τ_E was deduced.

The FST temperature T^* is defined to be the temperature at which the relation for $\tau(T)$ gives identical results for the fragile and the strong liquid. Its value turned out to be $T^* = 830 \pm 2$ K. Differences between the value of T^* deduced from the energy and the volume ACFs turned out to be within the statistical uncertainties.

B. Thermodynamic properties: Specific heat

The FST in BMG-forming melts [31, 32] and other glass-forming liquids [48] is often accompanied by a local maximum in the specific heat. Such a peak may be seen as an indication for a (smeared-out) thermodynamic phase transition (TPT). A TPT occurs at a point, where one phase (characterized, for example, by a [potentially multi-component] order parameter and/or the density) becomes more stable than another phase upon the change of an intrinsic thermodynamic variable, such as, temperature or pressure. TPTs are commonly classified according to the way how extrinsic variables change at the TPT. If one extrinsic thermodynamic variable changes discontinuously, the transition is called first order, while it is called a second-order transition when all extrinsic vari-

ables change continuously. In the latter case, “susceptibilities”, such as specific heat or compressibility, change discontinuously at the TPT or show integrable singularities without a δ -function contribution.

TPTs only occur in the thermodynamic limit ($N \rightarrow \infty$). In any finite system, there is always a finite probability for the system to peek into an unstable phase, even if this probability may be extremely small – and typically exponentially suppressed with (a sub-linear power of) the particle number N . Due to this exponential scaling, the thermodynamic limit is essentially always reached in experiments on bulk samples. This is different in computer simulations, where N often leads to a noticeable smearing out of the transition. The general rule is that the larger N , the less smeared out is the transition. Irrespective of the order of the transition, singularities or discontinuities occurring at a TPT are smeared out the more the smaller N . Similar comments should apply for a smeared-out TPT, for which correlation lengths do not diverge as in true TPTs, as long as the volume (mean size of the simulation cell) is less than the third power of a correlation length [37, 42].

Before studying the size dependence of the specific heat, we demonstrate in Fig. 3 that our largest studied model system has a local maximum in c_p . The form of the peak is reminiscent of experimental data in BMGs — see, e.g., Fig. 1(a) in Ref. 31 and Fig. 2(b) in Ref. 32 — but also in other classes of glass-forming melts — see Fig. 2(b) in Ref. 12. On the longest simulation time scales $t_{\text{sim}}^{\text{max}} = 2 \mu\text{s}$, which could be afforded for the largest system, equilibration could no longer be guaranteed for temperatures $T < 0.9T^*$, at which point our *in-silico* sample undergoes a glass transition, assuming an effective cooling rate of $\approx 10^7$ K/s at the smallest temperatures, i.e., 1 μs simulation time for each temperature, separated by roughly $\Delta T = 10$ K. Note that the specific heat due to the kinetic energy was included in Fig. 3, in order to facilitate direct comparison to experimental data.

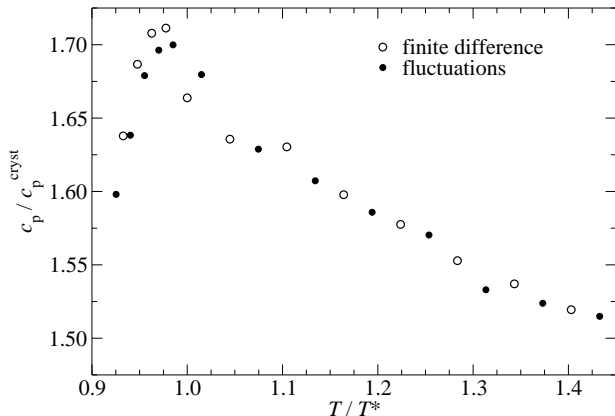


FIG. 3. Specific heat c_p of the $N = 8788$ -system as a function of reduced temperature T/T^* . c_p is scaled to the value that a classical harmonic solid would have, i.e., to $3 k_B$ per atom.

Small maxima in c_p are observed for any studied sys-

tem size N . However, in contrast to what should be expected from drawing an analogy to thermodynamic phase transitions, the maxima c_p^{max} decrease with increasing system size. The specific numbers are reported in Fig. 4.

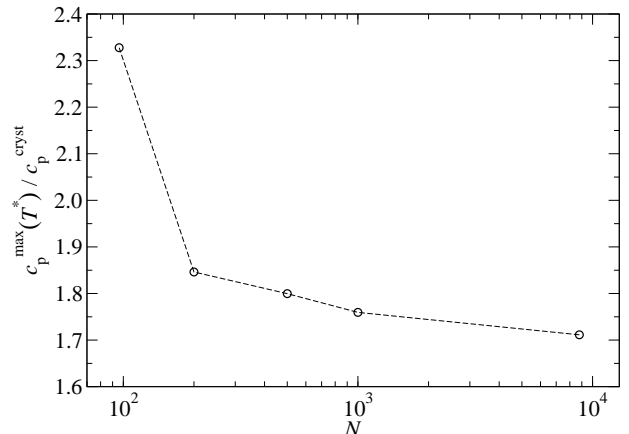


FIG. 4. Maximum value of the specific heat c_p at the FST as a function of particle number N . c_p^{max} is scaled to the value that a classical harmonic solid would have, i.e., to $3 k_B$ per atom.

The peak of c_p^{max} is particularly pronounced for the smallest studied system considered here, i.e., for $N = 96$. The number of $c_p^{\text{max}}/c_p^{\text{cryst}} \approx 2.3$ means the configurational specific heat (from which the excess specific heat originates) is enhanced by a factor of 3.6 w.r.t. to a harmonic solid. This can still be seen as a small number, yet, the “jump” in internal energy after integration over the peak is not entirely negligible, i.e., $\Delta U \approx 28 k_B K$ per atom, while that for the largest studied system is only $\Delta U \approx 4 k_B K$. Thus, the smaller systems show stronger signs of a TPT than the larger ones, which is the opposite trend of the generic features of TPTs. While we cannot offer a good explanation of the phenomenon beyond vague statements like the extensivity of entropy becoming valid at larger particle numbers than the extensivity of the internal energy, we feel that we can exclude the possibility of a simple phase competition at the FST.

C. Structural properties: Radial distribution function

To complete the analysis, we also investigated structural properties. Towards this end, the Zr-Zr radial distribution function (RDF) $g_{\text{Zr-Zr}}(R)$ is shown in Fig. 5, one time above and one time below T^* . For a general introduction to the structural evolution in BMG-forming melts, we refer to a recent review article [49].

If there were a competition between two different local structures, clear differences should appear between the RDFs below and above T^* . Changes in $g_{\text{Zr-Zr}}(R)$ for $N \geq 200$ remain almost undetectable when cooling from $T = 850$ K to $T = 800$ K. In fact, the RDFs super-

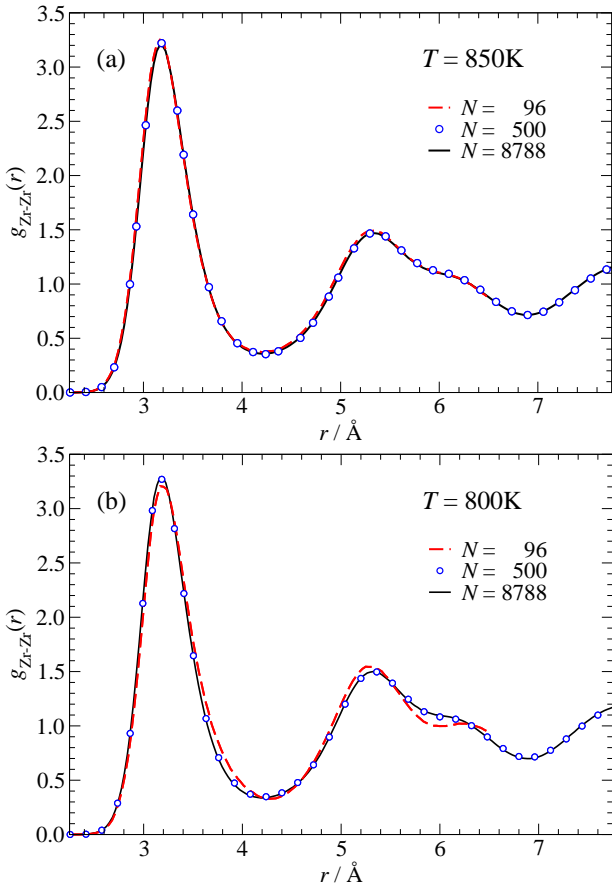


FIG. 5. The Zr-Zr radial distribution $g_{\text{Zr-Zr}}$ at $T = 850$ K above (a) and at $T = 800$ K below (b) the transition temperature $T^* \approx 830$ K.

impose within linewidth in the shown range when being multiplied with temperature. Only the $g_{\text{Zr-Zr}}(R)$ of the smallest system changes in a noticeable way. Specifically its second peak has more structure than the peaks of the larger systems, as revealed in Fig. 5b. This observation is again in contradiction to the expectations from TPTs, where smaller systems have less structure in the (usually but not always more ordered) low-temperature than in the high-temperature phase.

We assured that the transition for the $N = 96$ system did not (solely) arise due to a commensurability effect of some preferred local structures with the periodic boundary conditions of the cubic simulation cell. Towards this end, additional simulations were run at $T = 800$ K in which the $N = 96$ system was duplicated in each spatial dimension. The extra features in the eightfold system disappeared within less than 70 ns, while they had remained stable in the original, small system for more than 10 μs .

IV. CONCLUSIONS

In this work, we studied the fragile-to-strong transition in a bulk-metallic-glass forming melt using molec-

ular dynamics. The size dependence of c_p and of the radial distribution function were analyzed, after the used model had been shown to reproduce experimental results for the cross over from a non-Arrhenius to an Arrhenius-type dependence of dynamic properties and for the temperature dependence of the specific heat. The FST was found to be less sharp with increasing system size. In particular, the small $N = 96$ system revealed a much sharper peak in c_p at the FST and more structure in the Zr-Zr (and other not explicitly shown) RDFs below T^* than the larger, $N \geq 200$ systems. These observations contrast the expectations that arise from analogies to usual thermodynamic phase transformations. In the latter case, the specific heat increases with system size in the vicinity of a thermodynamic phase transformation, as long as the system volume is less than the third power of the correlation length of the order parameter driving the transition [37, 42].

An interesting observation was that the relatively sharp transition in the $N = 96$ system did not (solely) arise due to a potential commensurability or mismatch of a particular, preferred phase with the cubic cell shape. After duplicating the small, structured but yet equilibrated system at $T < T^*$ in all three spatial dimensions, the internal energy per atom increased to the value taken by the large systems and the detailed features of the RDF distinguishing the $N = 96$ from the $N \geq 200$ systems disappeared within a relatively short time span. We note that we made a similar observation for an even smaller system, namely $N = 48$, at a temperature very close to $T = 1,100$ K. As was the case for the $N = 96$ system near T^* , an apparent transformation of the small system disappeared after doubling the linear system size along all three spatial dimensions. At this higher temperature, RDFs and specific heat of the eightfold system was essentially indistinguishable from those of larger systems.

These observations make us conclude that volumes in the studied BMG-forming melt can only be seen as representative when they include more than $O(50)$ atoms at $T = 1,100$ K and more than $O(100)$ atoms at $T^* = 830$ K. These particle numbers, which should be expected to increase with decreasing temperature, will certainly depend on the system of interest and they could sometimes be difficult to reach with *ab initio* methods. Anyone simulating glass-forming melts in general and FSTs in particular, should surely confirm the considered volume to be representative.

A theoretical understanding of the transition should certainly reflect the sub-extensivity of the specific heat and latent heat of this and related (potentially even all other?) BMG-forming melts at the FST. A simple description of two competing phases within a mean-field-type picture does not appear to be consistent with our observations, even if the order parameter is allowed to have more than one component. It might yet be interesting to pursue the question what class of generalized Ginzburg-Landau theory (potentially with negative square-gradient corrections and higher-order stabilizing derivative terms)

can reproduce the thermodynamic anomalies of (bulk-metallic) glass-forming melts, even if the microscopic interpretation of the order parameter remains unclear.

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V. DATA AVAILABILITY

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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