Quasidiscontinuous change of the density correlation length at the fragile-to-strong transition in a bulk-metallic-glass forming melt

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Many bulk-metallic-glass (BMG) forming melts undergo a rather abrupt fragile-to-strong transition (FST), at which density and local structure appear to change only continuously. In this study, we reproduce similar results for a ternary BMG former ($Zr_{0.606}Cu_{0.29}Al_{0.104}$) using computer simulations. The results include a smooth evolution of radial distribution functions at small distances through the FST. However, the long-range density correlation length increases (quasi)discontinuously at the FST as revealed by an Ornstein-Zernike-based analysis of the radial distribution function. Likewise, the temperature derivative of $a_{Zr-Zr}(T)$ decreases (quasi)discontinuously at the FST. These observations add to the rich phenomenology of FSTs lacking a theoretical understanding.

I. INTRODUCTION

Glass-forming liquids frequently undergo a fragile-to-strong transition (FST) at which a high-temperature non-Arrhenius dependence of dynamical properties, such as shear viscosity and volume or energy relaxation times, crosses over to an Arrhenius-type dependence [1–11]. The FST often occurs in equilibrium well above the (experimental) glass-transition temperature T_g, e.g., in many bulk-metallic-glass (BMG) forming melts [8–10,12] and molecular glasses [2–6], but also in silica [6,7,13]. BMGs lacking a FST at conventional cooling rates revealed it when the cooling rate was much reduced [14]. The FST has even been observed in undercooled liquids, most notably water, outside thermal equilibrium [15–19]. It thus appears as if the FST is a common phenomenon of complex liquids defying crystallization.

In some cases, the FST is accompanied by significant structural changes resulting from the competition of two phases that differ clearly from one another, for example, through different densities [15,18]. A discontinuous change of the temperature dependence of dynamical properties is then not unexpected, but not necessarily an Arrhenius-like behavior at low temperatures and clear deviations from it at high temperatures. In contrast, when density evolves smoothly at the FST, significant structural changes in the local order at the FST have not been identified [12], which does not prevent the picture of two competing phases to be postulated [20].

The mode-coupling theory (MCT) explains a variety of dynamical anomalies, which occur at the FST [21–23], in particular, a high-temperature nonhopping dynamics not satisfying Arrhenius-like dependence to a thermally activated motion at low temperatures, in which (apparent) activation energies may differ for different elements at low T [7]. MCT assumes neither a competition of phases nor a (smeared-out) transition between them [22,23]. The FST in BMGs (and many other glass-forming melts) is nevertheless accompanied by thermodynamic anomalies such as a small but noticeable peak in the specific heat $c_p(T)$ just below the FST temperature T^* and a subsequent drop of $c_p(T)$ upon cooling to a value which is barely above that expected of a harmonic solid [12,24]. The small value of the specific heat is an indication of structural rearrangements with temperature being small or the melt jumping between different basins of attraction having similar energies. The presence of the peak in $c_p(T)$ is sometimes seen as an indication of a smeared-out phase transformation [24] or of the existence of two distinct disordered phases [14]. However, a recent simulation of a model BMG revealed that the peak height and intensity are subextensive, i.e., that it decreases with increasing system size [25]. This is the opposite of what should be expected from a competition between two different liquid phases.

The analysis of structural evolution in glass-forming melts in general and BMG-forming melts in particular has so far been focused on local two-point distribution functions [12,26–30] and on the analysis of the probability of locally preferred structural motifs to occur [26–29,31–38]. To the best of our knowledge, no (quasi)discontinuous changes in these properties was reported to exist at those FSTs lacking a density anomaly.

It appears counterintuitive that the quasicontinuous change of dynamics, which may even include a reduction of the apparent activation energies ΔE near T^* [9,14,27], does not correlate with similarly discontinuous structural changes. This motivated us to investigate not only the local radial distribution function in a BMG-forming melt but to focus on the asymptotic long-range density correlations. According to Ornstein and Zernicke [39] and subsequent work [40], these can be described as an exponentially decaying sinusoidal. To fill this gap, simulations were run on the alloy $Zr_{0.606}Cu_{0.29}Al_{0.104}$, which was recently demonstrated to reproduce the frequently observed local maximum of c_p just below T^* [25] along with some other features typical for FSTs of (bulk-metallic)-glass forming melts.

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The remainder of this paper is organized as follows: The model and methods are sketched in Sec. II. Section III contains the results and some discussion. Conclusions are drawn in Sec. IV.

II. MODEL AND METHODS

The model and the simulation setup used for this work are identical to those used in a former study [25], i.e., interactions in the considered model alloy $Zr_{0.606}Cu_{0.29}Al_{0.104}$ are described with an embedded-atom potential, which was carefully designed for Zr-Cu-Al ternaries [41]. Simulations are run again in the NpT ensemble using LAMMPS [42]. This time, the system size was fixed to $N = 8788$. Pressure is controlled again with a Nosé-Hoover chain [43] with a time constant equal to 1000 time steps, while temperature is maintained constant using a Langevin thermostat [44] with a time constant equal to 100 time steps. The time step was chosen to be 2 fs. We also took the liberty again to reduce the "isotope masses" of Zr and Cu to that of Al in order to collapse vibrational timescales of the different elements. While this isotope trick affects prefactors of dynamical properties, it leaves static observables as well as apparent activation energies unchanged because the Boltzmann distribution of a classical system factorizes into one term that solely depends on momenta and another one that solely depends on coordinates.

For the thermal treatment of the largest $N = 8788$ sample, we proceeded as follows: The alloy was set up on an fcc lattice, chemical identities and vacancies were assigned randomly, and the resulting configuration was simulated for 100 ns at the highest temperature of $T = 1200$ K. The following steps were then repeated each time the temperature was set to a new value. First it was ensured that the instantaneous energy clearly fluctuated about its (new) mean value. Towards this end, the energy measurements were passed through a low-frequency filter, which was necessary to do because the energy distribution functions obtained at "adjacent temperatures" overlapped within a standard deviation. The equilibration times turned out *a posterio* to be 10 times the energy autocorrelation time τ_E for T clearly above T^* and more than $100 \tau_E$ in the vicinity of T^*. The final configuration was then used as initial input for the observation simulation at the same temperature (running over time periods exceeding that of the relaxation by at least a factor of two). It was also used as input for the next lower temperature. Temperature jumps were 50 K at $T > 900$ K and 25 K at smaller temperatures. Near T^*, additional simulations were run to obtain better resolution, i.e., the temperature discretization was further reduced to 12.5 and 8.5 K. For these additional runs, configurations were sometimes taken from the nearest higher or from the nearest lower temperature. This was done to explore if there was any (systematic) deviation on final results, e.g., in the form of a hysteresis, depending on whether configurations had been cooled or heated. In addition, we occasionally checked if the Ornstein-Zernike (OZ) analysis conducted on the configurations of the last half of the relaxation run would only necessitate a single pole to describe the density oscillations at $T > 12.5$ Å.
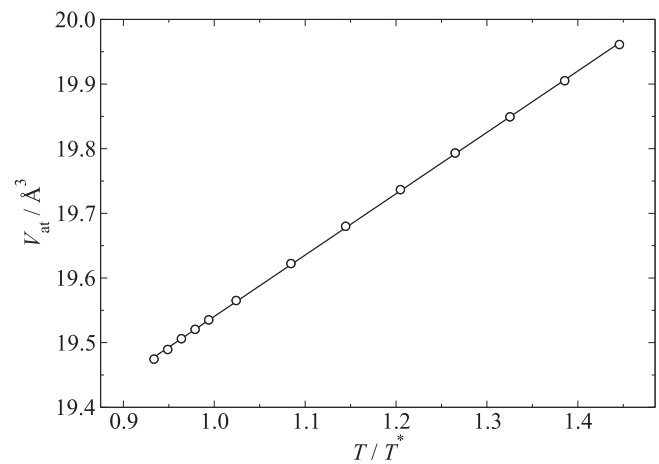

FIG. 1. Volume per atom V_{at} as a function of temperature T, which is normalized to our estimate for the FST temperature of $T^* = 830$ K. The straight line is a linear fit to the simulation results.

Smaller systems, most notably with $N = 1000$ atoms, were also simulated. For the smaller systems, the number of relaxation steps was set to five times those used in the large system.

The structure was studied using the conventional radial distribution function $g(r)$, which states the probability density to find an atom a distance r from a given atom in units of the number density ρ_0, so that $g(r \to \infty) = 1$. The long-range density fluctuations are better analyzed using a modified pair-correlation function defined as

$$G(r) \equiv 4\pi r^2 \rho_0 \{g(r) - 1\}. \quad (1)$$

Its sine transform is proportional to the static structure factor [45].

III. RESULTS AND DISCUSSION

In our previous study [25], we established a (quasi)discontinuous change of the apparent activation energy deduced from the volume and energy relaxation time $\tau_{V,E}(T)$ of our model alloy at $T^* = 830 \pm 2$ K. Specifically, while $\tau(T)$ was continuous, the apparent activation energy $\Delta E_{V,E} \equiv \partial \ln \tau_{V,E}(T)/\partial \beta$ with $\beta = 1/k_B T$ changed quite abruptly at T^*. At the same time, it was found that the peak and the intensity of the specific heat $c_p(T)$ at T^* decrease with increasing system size, providing evidence against the interpretation of the FST to result from a simple competition between two phases. In this paper, we present an analysis of the structural changes accompanying the FST.

A. Temperature-induced structural changes in local order

Abrupt changes in activation energies could, in principle, be induced by abrupt structural changes. The simplest quantity defining structure is the mean number density or its inverse, the volume per atom, which we denote as V_{at}. Its temperature dependence is displayed in Fig. 1. No discontinuities in $V(T)$ or in the thermal volume expansion coefficient $\alpha \equiv \partial \ln V/\partial T$ become obvious within the statistical uncertainty of the data. One immediate consequence of this observation is that it should be difficult to identify a meaningful relation

between the so-called free volume (whatever this quantity is precisely meant to be) and the relaxation times in the considered melt.

A change of the thermal-expansion coefficient near the FST had been reported earlier [27] from a molecular dynamics model similar to ours. We believe that this conclusion was a consequence of the large cooling rates, which were effectively 0.5 K/ps—similar to those used in many other simulations of quenched BMGs [37]. This moved the *in silico* T_g to the immediate vicinity of T^*. In fact, with equilibration times of $O(1 \, \mu s)$ near T^*, we only just managed to equilibrate the melts (using jumps of 12.5 K near T^*) at an effective cooling rate of approximately 10^7 K/s, while the former study equilibrated only for 100 ps after temperature changes of 100 K were followed by a 3.4 ns lasting temperature holding process. T^* and T_g would no longer have been resolved from one another with such large temperature jumps, even if the relatively large relaxation times of 1 μs had been used. We thus argue that the (very interesting and well conducted) study by Zhang *et al.* [27] investigates the FST in a supercooled liquid in which T_g and T^* are close to each other. In fact, when we initially equilibrated our samples for shorter times, we also observed a change of thermal expansion at T^*.

We claim our system to be in thermal equilibrium, which we ensured as follows: (i) getting similar numbers for the specific heat from energy fluctuations and from the finite difference of the internal energy, and (ii) reproducing the correct asymptotics of the long-range density fluctuations (LRDFs) in the melt. Usually, the LRDFs deviate noticeably from the Ornstein-Zernike asymptotics during relaxation after a temperature reduction in the melt; see also Eq. (3). Of course, deep in the glass, specific heats from fluctuations and finite difference match up again. Likewise, the long-range structure in glasses may reflect the fluctuations that existed in the equilibrium phase just above the glass transition [46]. However, while going through the glass transition, both tests should produce results that deviate from those expected for an equilibrium system.

A smoothly evolving density does not necessarily imply a smoothly evolving local structure since two distinct structures may still have a similar density. The most generic way to characterize local order is through the radial distribution function $g(r)$. The partial $g(r)$ related to Zr atoms is shown in Fig. 2 at a temperature just above and another temperature just below T^*. No changes can be resolved in the shown range of r. A similar comment applies to all other partial radial distribution functions including the mixed ones, which are not shown explicitly.

Another local quantity, which has recently enticed some interest in the literature [28,47–50], is the mean-bond length a. In principle, a is difficult to define in a liquid since no reference positions of atoms exist as in crystals. Even in crystals, there is overlap between the nearest- and next-nearest-neighbor peak in $g(r)$, making an accurate determination of instantaneous bond lengths (which exceeds the ones associated with the crystallographic positions due to thermal fluctuations normal to the bond) from the analysis of $g(r)$ alone inaccurate. In order to better define local bonding and to discriminate between contributions from first and more distant neighbors, Voronoi tessellation can be made. Recently,
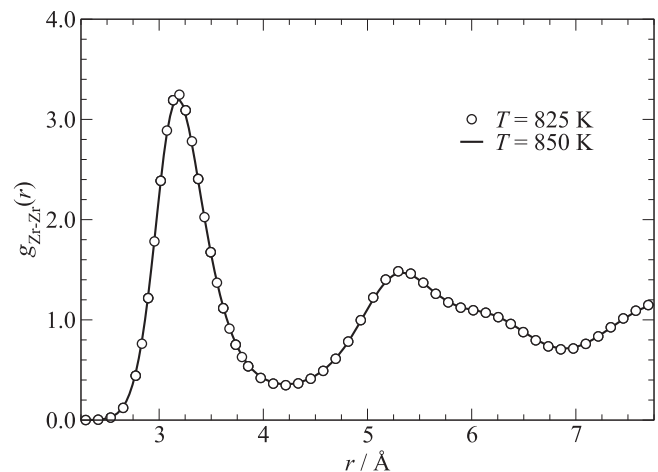

FIG. 2. Zr-Zr radial distribution function for two temperatures: one above ($T = 850$ K) and one below ($T = 825$ K) the FST temperature.

we demonstrated that the mean bond lengths deduced from Voronoi tessellations and that of a skewed-normal-distribution (SND) analysis of the first peak of the radial probability density defined as

$$\mathrm{Pr}(r) \equiv 4\pi r^2 g(r) \rho_0 \qquad (2)$$

match much more closely than those deduced from averaging the bond length up to, say, the first minima in either $g(r)$ or $P(r)$ (the integral over which states the average number of neighbors contained in the shell) [49]. An example of such a SND analysis is shown in the inset of Fig. 3, while the mean bond length deduced from such analyses is shown in the main panel as a function of temperature. The $a_{\mathrm{Zr-Zr}}(T)$ relation for the smaller $N = 1000$ sample (not shown) was essentially indistinguishable from that of the $N = 8788$ system, although
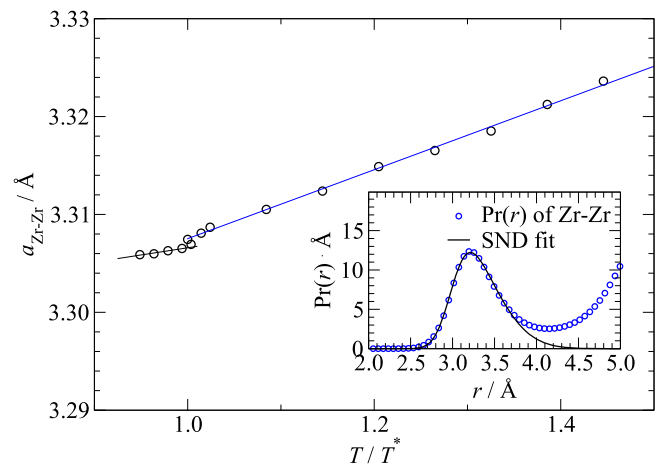

FIG. 3. Main panel: Zr-Zr nearest-neighbor distance $a_{\mathrm{Zr-Zr}}$ obtained by a SND analysis. Straight lines are linear fits to the simulation data above and below T^*. The temperature is normalized to our estimate for the FST temperature of $T^* = 830$ K. Inset: Example of a SND analysis performed on the first peak in the radial probability density $\mathrm{Pr}(r)$.

it had been cooled at a rate effectively five times smaller than the large sample.

Figure 3 reveals that the thermal expansion of the mean bond length is considerably reduced in the strong phase as compared to the fragile phase. This observation supports previous interpretations of experimental x-ray spectra obtained for a five-component BMG [12] having a similar relative number of the dominating Zr and Cu atoms as our model alloy. However, the bond expansion coefficient remains positive also at $T < T^*$, while previous works deducing bond lengths and neglecting overlap effects of adjacent peaks in $g(r)$ found it to be negative [28,47,48]; see also the thorough discussion of this issue in a recent review article [50].

At this point, we cannot yet convincingly explain how a kink in $a(T)$ can have so little effect on $V(T)$. However, a first hint can be obtained from the simulations by Zhang *et al.* [27], who conducted a careful Voronoi analysis of a BMG forming melt. They found asymmetry in the Voronoi polyhedra to suddenly increase above T^*. Such a structural change can lead to a change of mean bond lengths without affecting volume. The simplest case to illustrate this argument is to consider a perfect square lattice, in which one atom is moved a small distance parallel to a diagonal. This preserves the total volume, but increases the mean bond length.

B. Temperature-induced structural changes in long-range order

Following results of Ornstein and Zernicke [39], density correlations in three-dimensional liquids (with sufficiently quickly decaying direct atom-atom interactions) can be described as a superposition of damped sinusoidal functions [40] according to

$$G(r) = \sum_l G_l \, r \, e^{-r/\zeta_l} \cos(k_l r - \varphi_l), \tag{3}$$

where G_l is a parameter of unit inverse squared length, ζ_l a correlation length, k_l is a wave number, and φ_l is a phase. The asymptotic behavior at large r is dominated by the summand l having the largest correlation length ζ_l. In nonmonoatomic fluids, the asymptotic behavior is described by the same complex wave number $q_l = k_l + i/\zeta_l$, while the parameters G_l and φ_l must be indexed with the respective atomic indices [51]. As mentioned in Sec. II, we focus on $G(r)$ [see also Eq. (1)] rather than on $g(r)$ because $g(r)$ has poor resolution at large r.

Several radial distributions $G(r)$ were measured for different atom pairs, i.e., Zr-Zr, Zr-Cu, and Cu-Cu, in the same way as presented exemplarily for Zr-Zr at two different temperatures in Fig. 4. Within (small) stochastic uncertainties, the location of the complex wave numbers (or "poles") $q_l = k_l + i/\zeta_l$ was identical for all considered correlation functions. Since statistics are best for Zr-Zr in our alloy, it was decided to present results on that atom pair in the following.

It can be observed that the (temperature-scaled) functions $G(r)$ shown in Fig. 3 superimpose within line width up to a distance of, say, $r \approx 15$ Å. However, they become distinct at large separation, i.e., the decay length is apparently slightly increased for the temperature just below T^* as compared to that just above T^*. A more detailed analysis of the temperature dependence of the asymptotic decay length ζ is shown next in Fig. 5.

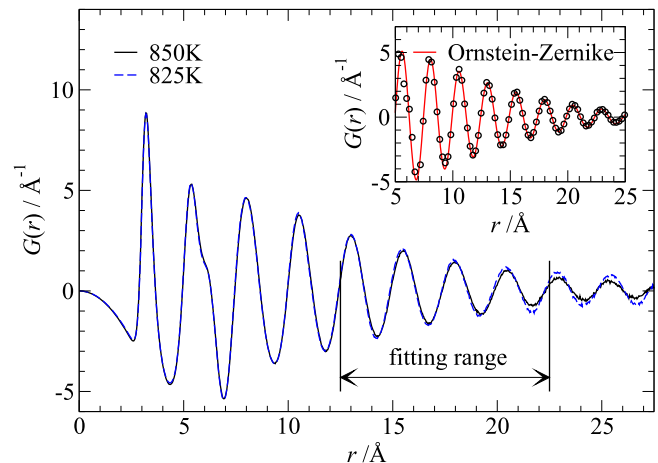

FIG. 4. Temperature-scaled $G(r)$ for two temperatures: one above and one below the FST. Inset: Fit of $G(r)$ at $T = 850$ K. Symbols represent simulation data, while the lines are produced using the asymptotically dominant term on the right-hand side of Eq. (3).

In contrast to all other properties considered so far, the density correlation length ζ changes discontinuously near T^*, when temperature is resolved with $\Delta T = 12.5$ K. Usually, we would have considered such a change to be a clear indication of a first-order phase transformation, which might potentially be smeared out. Since a previous analysis of the specific heat revealed subextensivity [25], we can exclude the possibility of a first-order thermodynamic phase transformation and by extension exclude the possibility of a true discontinuity of any property as a function of temperature [52]. We therefore also argue that the transition of ζ through the FST has to be continuous. Indeed, a more refined temperature grid near T^* reveals the crossover to be continuous.

Our study is not the first one to report a sudden change in the long-range density correlations at a given temperature. Experiments on binary hard-sphere mixtures revealed similar phenomena with changing composition—rather than
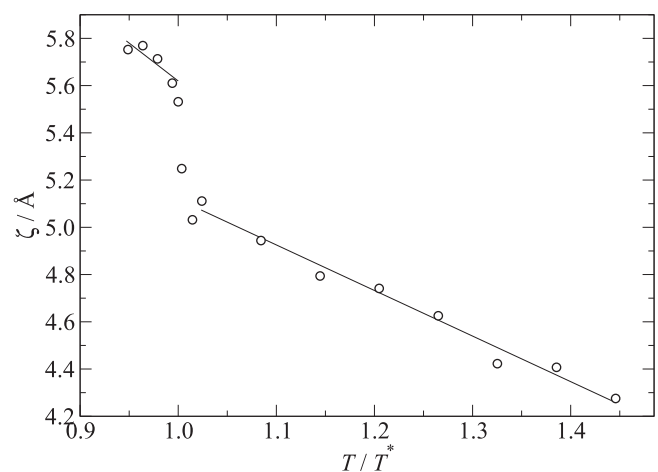

FIG. 5. Correlation length of the long-range density fluctuations as a function of reduced temperature. Lines are fits to data above and below T^*.
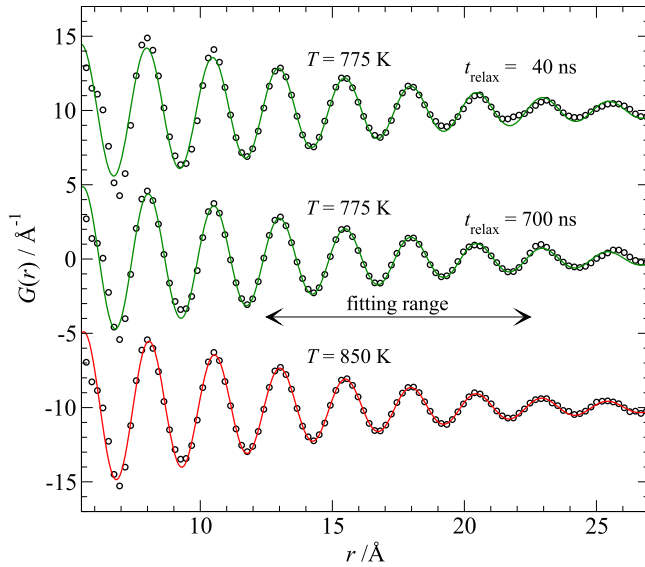
FIG. 6. Example for a temperature-scaled $G(r)$ deduced from a sample that had only been partially equilibrated at $T = 775$ K, one time by 40 ns and one time by 700 ns. Data for an equilibrated sample at $T = 850$ K, which is identical to the one shown in the inset of Fig. 4, is included here to compare the data quality. OZ fits cover the same range of distances as in Fig. 4 (green lines for $T = 775$ K, red line for $T = 850$ K). Note that the symbols only reflect every seventh data point. Other data points were skipped to facilitate the comparison between OZ analysis (lines) and simulation data (circles).

with temperature [53]. Statt *et al.* [53] demonstrated that this crossover could be rationalized without having to postulate a phase transition. If the long-range asymptotics are described with a two-pole approximation to $G(r)$, the imaginary part of the two poles can be identical at the same temperature T' while their real parts differ. Thus, one pole is asymptotically dominant above T', while the other is dominant below T'. This scenario clearly does not apply to our system, as the correlation length (i.e., the imaginary part of the complex wave vector) is discontinuous, while the real part is continuous. For our system, the sudden change of $G(r \to \infty)$ at T^* is not due to one pole becoming more important than another one.

C. Density correlations during relaxation

While the analysis of nonequilibrium systems is not part of this study, we wish to corroborate our claim that the long-range density oscillations deviate noticeably from the Ornstein-Zernicke asymptotics during relaxation after a temperature reduction in the melt. Towards this end, we present data on $G(r)$ at the lowest temperature, namely, $T = 775$ K, which was simulated but not deemed sufficiently equilibrated to be included in the equilibrium data of this work.

The sampling for Fig. 6 was done as follows: The initial configuration was taken from $T = 787.5$ K and equilibrated at the new temperature over 40 ns and then for another 660 ns. These numbers need to be set into relation with the (estimated) energy-correlation time of 15 ns, as deduced from the data presented in Fig. 2 of Ref. [25]. $G(r)$ was averaged over the time intervals $40 < t < 80$ ns and $700 < t < 740$ ns,

respectively. The agreement between OZ asymptotics and measurement turns out noticeably less satisfactory than in the inset of Fig. 4, which had also been averaged over 40 ns, however at $T = 850$ K. While symbols and fits overlap within symbol size in the range $10 < r < 25$ Å in the equilibrated $T = 850$ K sample (our admittedly somewhat arbitrary extra criterion for equilibration to be satisfactory), this is not the case for the $T = 775$ K system. After the relatively short relaxation time of $t_{relax} = 40$ ns, which is still almost three times τ_E, the OZ fit already fails at relatively short distances, while the first clear discrepancies move to larger values of r for $t_{relax} = 700$ ns, disregarding, of course, the deviations between fit and MD data at small r, where density correlations are not yet dominated by a single pole.

It may seem pedantic to judge the OZ analysis of the $t_{relax} = 700$ ns as a sign of insufficient equilibration, as the green line is only marginally outside the symbol size for $r > 25$ Å. However, we noticed that the values of ζ deduced from fits of the given quality can lead to errors of more than $\Delta\zeta = O(0.2$ Å$)$. The observed need for excessively large relaxation times is in line with the realization by Coslovich *et al.* [54] that producing true equilibrium values of certain properties, e.g., for the specific heat, can require equilibration times of more than $100 \, \tau_E$.

IV. CONCLUSIONS

Using molecular dynamics, we investigated structural changes—particularly as characterized through the modified radial distribution function $G(r)$—at the fragile-to-strong transition (FST) in a bulk-metallic-glass forming melt. We identified a (quasi)discontinuity in the density correlation length ζ at the FST temperature T^*, where ζ abruptly increased by $O(10\%)$ upon a $O(1\%)$ temperature change upon cooling. Above and below T^*, an $O(1\%)$ temperature increase induced only an $O(0.3\%)$ decrease of ζ. Such a clear signal would usually have to be interpreted as a first-order phase transition because a discontinuous change in $G(r)$ implies a discontinuity in (two-body) entropy [55]. What prevents us from drawing this conclusion is that local changes in $G(r)$ could not be ascertained at the FST and, more importantly, a former study found the specific heat to be subextensive [25].

The particle numbers beyond which the subextensivity of the specific-heat peak of our system becomes small is $N \approx 200$, which translates roughly into a system size of 4 nm³. This volume is close to the one of a cubic cell having a linear dimension equal to three times the correlation length, in which case an atom i sitting halfway between another atom j and its first periodic image j' has a distance of 1.5ζ to either one. A possible—and certainly speculative—explanation of the subextensivity of c_p resulting from the $G(r)$ analysis is that a cluster with a radius of the liquid correlation length behaves solidlike. Only the coupling to a liquid in a larger cell prevents or significantly reduces the tendency of the central cluster to undergo a process akin to a phase transformation. If this speculation were true, a large peak in the specific heat at the FST should go hand in hand with a larger liquid correlation length ζ.

It also seems as though periodically repeated finite systems show a peak in the specific heat at the temperature where the

linear cell size L is slightly larger than twice the correlation length ζ. In our previous work [25], the $N = 96$ sample with $\langle L \rangle = 12.33$ Å had a distinct maximum just below T^*, where $\zeta \approx 5.6$ Å $= 0.454\langle L \rangle$, while an $N = 48$ sample with $\langle L \rangle = 9.74$ Å revealed a maximum at $T = 1100$ K, where $\zeta \approx 4.4$ Å $= 0.452\langle L \rangle$. In contrast, larger systems did not reveal any anomalies at 1100 K. Thus, a small system could appear to undergo a (smeared-out) transformation simply because ζ is roughly half the linear size of the simulation cell.

Finally, we wish to note that we believe that an Ornstein-Zernike-based analysis can be beneficial for the study of complex liquids and should actually be routinely used for this reason: first, it allows the simulator to ensure that the system is large enough (i.e., the linear dimension of the cell should be ideally at least three times the correlation length ζ) to be meaningful, but not wastefully large so that—assuming a fixed computational contingent—the smallest possible quenching rates can be studied. Second, the Ornstein-Zernike analysis is a reliable tool to ensure that (metastable) equilibrium is reached. After a short, but of course not too short, relaxation, we always observed clear differences between the analytical asymptotic form and simulation results. Agreement always necessitated long, and at the lower temperature painfully long, equilibration of the samples.

ACKNOWLEDGMENTS

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