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Reply to "Comment on 'Rapid chemical and topological ordering in supercooled liquid $Cu_{46}Zr_{54}$'"

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The criticisms of Harvey and Gheribi (HG) are directed towards supporting evidence for ordering in supercooled $Cu_{46}Zr_{54}$ liquid from specific heat measurements and molecular dynamics simulations, not on the direct evidence that came from x-ray diffraction studies. In this reply, we demonstrate that the unique features observed in the specific heat [*Cp(T)*] are not artifacts of any specific assumptions, as suggested by HG. We have furnished additional details of the MD simulations and clarified related issues raised by HG. The basic conclusions, however, remain unchanged.

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It is important to emphasize that the central point of our recent paper[1] on $Cu_{46}Zr_{54}$ was the unusual temperature dependence of the total pair distribution function $g(r)$ (Figs. 3 and 4 in the original publication) in the supercooled liquid. Previous experiments on amorphous alloys[2,3] and simulations of liquids[4–6] have demonstrated that the first peak in $g(r)$ is split, due to a mixture of short- (Cu-Cu), intermediate- (Cu-Zr), and longer-distance (Zr-Zr) partial pair correlation functions. Our liquid data show that the smaller-r maximum in the split first peak of $g(r)$ grows at a faster rate relative to the other below approximately 850 °C (75 °C below the liquidus temperature). Irrespective of any additional data, a natural conclusion from this observation is that the liquid is undergoing rapid chemical ordering below this temperature. This chemical ordering correlates with topological ordering in structural models constructed from Reverse Monte Carlo (RMC) fits to the diffraction data, and it is consistent with molecular dynamics (MD) simulations of this liquid, performed by us[7] and independently by others.[4] No *experimental* study to our knowledge has previously found the high degree of coordinated chemical and topological ordering in a metallic-glass-forming liquid that is reported in our paper. However, Harvey and Gheribi (henceforth referred to as HG) do not mention this fundamental experimental observation in their criticism of our work. Instead, their criticism is directed toward the supporting evidence from specific heat, thermal expansion coefficient, and molecular dynamics simulation studies.

The first issue raised by HG is with regard to the constant-pressure specific heat $C_p(T)$ in the equilibrium and supercooled liquids, which was estimated by assuming a *temperature-independent total hemispherical emissivity* $\varepsilon = 0.25$ [it was mistakenly stated that $\varepsilon = 0.2$ in the paper; see Erratum (Ref. 8)]. It is important to point out that it was clearly stated in the original paper that ε was assumed to be temperature independent. This assumption makes the presentation of the data in the forms of $C_p(T)$ and $C_p(T)/\varepsilon$ equivalent, except for a constant dividing factor. HG also mention the thermophysical property measurements of liquid $Cu_{50}Zr_{50}$ made by Fan *et al.*[9] We showed[10] HG that by assuming a reasonable value for ε (0.25), the data in Ref. 9 give a value of approximately 167 J mol^{-1} K^{-1} for C_p at 1200 K (near the liquidus temperature), which is greater than $20R$, where R is the molar gas constant. The specific heats of liquids rarely exceed $4R$ to $5R$. An unrealistically small value for ε would be required to bring the data in Ref. 9 into agreement with expectation. Such a large discrepancy indicates that our data are more reliable. We completely agree with HG, however, that a temperature-independent emissivity is not fully justified, and clearly stated so in the original paper. We now examine the consequences if other reasonable assumptions for $\varepsilon(T)$ are made.

The central question is whether the key feature of $C_p(T)$ would have remained were $\varepsilon(T)$ known. This is the onset of a greater rate of increase in $C_p(T)$ with decreasing temperature that begins at the same temperature where the anisotropy in the first peak in $g(r)$ begins to develop. This is the primary reason that the $C_p(T)$ data were included in the original paper. Because $\varepsilon(T)$ data are not available for liquid $Cu_{46}Zr_{54}$, it is necessary to use data for other liquid alloys. With HG, we investigated[10] the robustness of this feature and of the reported maximum in $C_p(T)$ by using $\varepsilon(T)$ data measured for $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$,[11] given by

$$\varepsilon(T) = 0.284 - 2 \times 10^{-4}(1100 - T),$$

where T is the temperature in °C. HG have chosen to place those results in Fig. 1 of their Comment (the "modified" data). We do not believe that these data are a fair representation of the temperature dependence of C_p for $Cu_{46}Zr_{54}$, as was conveyed in Ref. 10. They were presented to HG as a worst-case scenario (for reasons outlined below) to demonstrate that the features in the $C_p(T)$ data that were presented in our original paper as support for the structural data remained valid. That is not mentioned in their Comment. There are several reasons to mistrust this choice of $\varepsilon(T)$ to describe liquid $Cu_{46}Zr_{54}$. First, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ is a very

TABLE I. Temperature coefficients of emissivity for various elemental solids.

Element	Temp. coeff. of $\varepsilon(T)$	Source and notes
Cu	2.2×10^{-5}	Ref. 12
V	9.62×10^{-5}	Ref. 13
Nb	7.37×10^{-5}–1×10^{-4}	Refs. 14 and 15
Mo	9.86×10^{-5}–1.15×10^{-4}	Ref. 16, calculated Ref. 15, average of many sources
Ta	1.85×10^{-4}	Ref. 17
Hf	4.79×10^{-5}	Ref. 18, calculated

different liquid from the one that we are studying. Second, $\varepsilon(T)$ was *calculated* by matching the $C_p(T)$ data from differential scanning calorimetry (DSC) measurements made near and below the glass transition temperature to data obtained from electrostatically levitated samples, using measured emissivity data at only one temperature above the liquidus temperature.[11]

In the essentially complete absence of experimental data for $\varepsilon(T)$ for glass-forming alloy liquids, it is only possible to assume a realistic value for $\varepsilon(T)$ based on available data for elemental metals. It should be noted that, compared to spectral emissivities at a few discrete wavelengths, the experimental data for temperature dependence of total hemispherical emissivity are scarce even for elemental transition metals. The temperature coefficients for the total hemispherical emissivity have been measured for some *solids* at high temperature; these are summarized in Table I.[12–18] The magnitude of ε scales with the magnitude of the electrical resistivity for metals (see Ref. 19 and the numerous papers cited there). Since the temperature coefficient of resistivity for liquid metals is smaller than for crystalline metals, the temperature coefficient for $\varepsilon(T)$ should also be smaller for liquids than for solids. This is the case for Nb, for example, where the temperature coefficient for the liquid is in the range $(0.72–2) \times 10^{-5}$, while that for crystalline Nb is almost an order of magnitude larger (Table I and Ref. 20). The temperature coefficient of $\varepsilon(T)$ is expected to be even smaller in metallic alloy liquids for the same reason. Taking account of all these factors, a realistic value for the temperature coefficient for $\varepsilon(T)$ for the $Cu_{46}Zr_{54}$ liquid should be less than 1×10^{-4}. Shown in Fig. 1 of this Reply is $C_p(T)$ calculated by assuming this more realistic value, given by

$$\varepsilon(T) = 0.25 + 1 \times 10^{-4}(T - 925),$$

where T is the temperature in °C, and the original data (ε = const = 0.25). As expected, the increase in $C_p(T)$ with decreasing temperature is smaller for the corrected data. However, the abrupt rise and plateau survive, although becoming broader. It is important to point out that even with the unrealistic values for $\varepsilon(T)$ assumed in our correspondence with HG ("modified data" in their Fig. 1) hints of these features still survive, with $C_p(T)$ increasing suddenly between 800 and 850 °C. However, as will be discussed later in this Reply, we do acknowledge that the sharp decrease in $C_p(T)$ that is observed in one set of experimental data presented in our original paper may be questionable.

We strongly disagree with HG that C_p for a metallic liquid should decrease with temperature in the supercooled state. Their suggestion that liquid $Cu_{47}Ti_{34}Zr_{11}Ni_8$ (Refs. 9 and 10 in HG) and $Pd_{77.5}Cu_6Si_{16.5}$ show a decrease in C_p with temperature should be taken with caution. Neither of the reports that they cite contain data measured from supercooled liquids. From the DSC measurements made near T_g and a few data points above the liquidus temperature, an extrapolation was made, which, in our judgment, is unreliable. It is in conflict not only with our data, but with that of many others, who have shown an increasing C_p with decreasing temperature in supercooled glass-forming metallic alloy liquids.[21–26] That behavior has also been reported for a few elemental metallic and semiconducting liquids,[27] and liquid Ar.[28] Collectively, all of the evidence argues that the decrease of $C_p(T)$ with decreasing temperature (HG Fig. 1) results from the use of an inappropriate assumption for $\varepsilon(T)$. It should also be noted that this rise in C_p with cooling is expected. It indicates a rapid decrease (faster than expected from the temperature change) in enthalpy, which has been associated with a rapid development of structural order in close-packed systems.[29,30]

HG raise additional concerns about the density and thermal expansion coefficient data. The temperature dependence of the

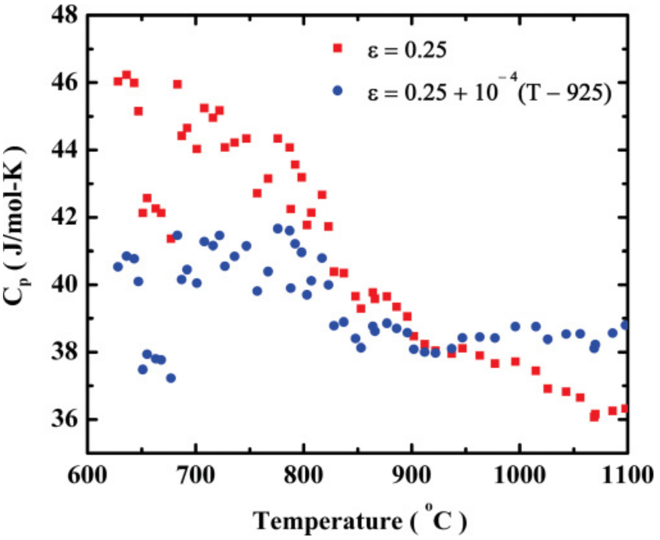

FIG. 1. (Color online) Experimental data for $C_p(T)$ for one cooling cycle from Ref. 1, showing the original calculation using constant emissivity [$\varepsilon = 0.25$ (red squares)] and calculated using a more realistic value [$\varepsilon(T) = 0.25 + 1 \times 10^{-4}\ (T - 925)$, blue circles]; the distinct rise and plateau in $C_p(T)$ are present in both cases, indicating that these features are not artifacts of the assumptions for $\varepsilon(T)$.

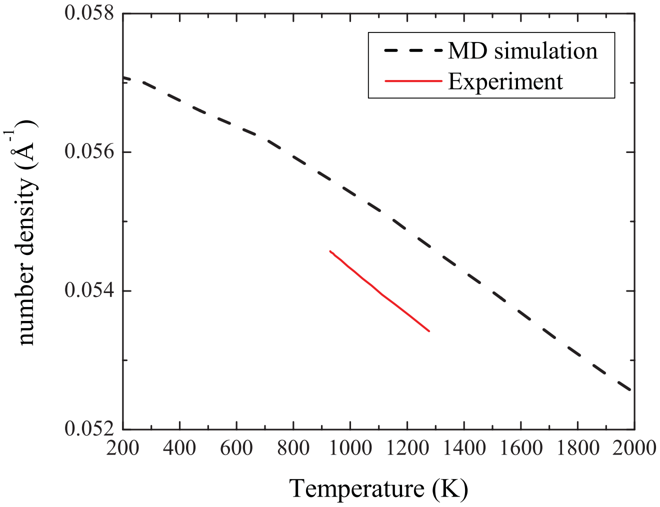

FIG. 2. (Color online) A comparison of the number density from experiments (red line, data presented in Ref. 1) and MD simulations (black dashed line); the densities agree within about 3%.

density can be described by a linear behavior as they suggest. However, small changes in slope in a quasilinear function cannot be observed from such fits, motivating the fit to the low- and high-temperature data separately, as was presented in our original paper. A small, but significant, difference in slope was observed. To answer HG's objection that "no particular physical or chemical phenomena would justify this anomaly," this could be consistent with the observed chemical ordering if the anharmonic contribution to the expansivity in the ordered phase were larger than in the high-temperature structure. This was only a suggestion; it was not based on incontrovertible experimental evidence. The argument of ordering did not hinge in any way on this small change in expansivity, but the apparent correlation was sufficiently interesting to point out. The measured density data are shown again in Fig. 2 of this Reply, with the densities obtained from the MD simulation. They are in qualitative agreement (to within approximately 3%).

HG discuss a relationship between our observations and the glass transition. Since no suggestion was made in our paper to connect any of the observed anomalies with a glass transition, those considerations are not directly relevant to the central theme of the paper. However, we do recognize that there was ambiguity in the original paper regarding this point in the discussion of the MD results. This is addressed later in this Reply. In our paper, we suggested a fragile-strong transition as one of *several* possible explanations for our observations. A reason for singling this one out is that such a transition has been reported recently in another Bulk Metallic Glass (BMG)-forming liquid,[31] based on measurements of the viscosity. Our structural measurements in $Cu_{46}Zr_{54}$ provide a motivation for similar viscosity measurements to be made in that liquid, since together they could deepen the understanding of transitions in supercooled liquids. That suggestion, made at the end of the paper, was in no way a central theme of our paper.

HG raise concerns about the results of the MD simulations and their comparison to the experimental data. They suggest that the number of parameters used to specify the Cu-Zr potentials represents an overly complex fitting. In fact, the potentials were constructed using spline tabulations of the relevant embedded-atom functions, which is common practice.[32] These spline tabulations are not unique—a function may be specified accurately using a number of different tabulations. The potentials used were developed previously for a different system ($Cu_{65}Zr_{35}$) than the one used in experiments ($Cu_{46}Zr_{54}$), and no fitting or direct input of the experimental data for $Cu_{46}Zr_{54}$ was made here. Rather, the potential had been tuned to reproduce certain physical parameters such as melting temperature and crystal phase formation, as well as properties of the liquid phase, in $Cu_{65}Zr_{35}$. *Ab initio* simulations[33] may show strong compositional changes due to electronic structure effects, which may not be captured properly in the empirical potentials, if they were not developed to match those effects. The potential used has been shown to adequately reproduce qualitative structural trends, including the liquid structure factors,[7] for a wide range of Cu-Zr compositions and is consistent with *ab initio* results.[34] Of course, much simpler and intuitive models of the liquid energy may be developed to fit the thermodynamic information. However, this was not our goal. Rather, it was to test the *predictive* power of the MD simulations, with respect to qualitative trends in the supercooled liquid structure, using *existing* interatomic potentials. Based on these considerations, as well as technical ones such as the large difference in cooling rates between experiments and MD simulations, we do not believe that a detailed, quantitative comparison between our experimental and MD results is productive. However, a valid concern raised by HG regards our oversight of not providing units for the MD-calculated C_p, which made a quantitative comparison to the experimental data impossible. A revised, quantitative presentation of these data is provided in Fig. 3. It should also be noted that the potential used in the original paper was, in fact, developed more recently than originally stated (in Ref. 5 instead of Ref. 35).

To provide further information about our MD calculations, the system was continuously cooled, using either the well-known LAMMPS code, or our own code, under constant pressure and temperature conditions. Cooling rates of 5×10^{10} and 5×10^{11} K/s produced very similar results for energy vs temperature; the results from different codes were essentially identical. $C_p(T)$ was calculated by taking a numerical derivative of the running-average energy with respect to temperature. Thus, an explicit functional form was neither needed nor used for this analysis.

From Fig. 3, it is evident that the published C_p obtained from our MD calculations is systematically smaller than the values obtained experimentally. An explanation of this discrepancy would require, in the least, detailed knowledge of the emissivity (see earlier discussion), and is thus outside the scope of this work. Moreover, the quantitative behavior depends upon the potential as well as the cooling protocol, as HG point out. Both the experimental and MD results show a rapid rise in $C_p(T)$ and a subsequent plateau or maximum around 700 °C. The MD data and one set of the experimental data show a distinct peak, a point that HG contest. As mentioned earlier, we agree that the sharp maximum shown in one data set ("experiment 2" in Fig. 3, indicated by the hollow red squares) is questionable. However, this is not because of the assumption of a temperature-independent emissivity as

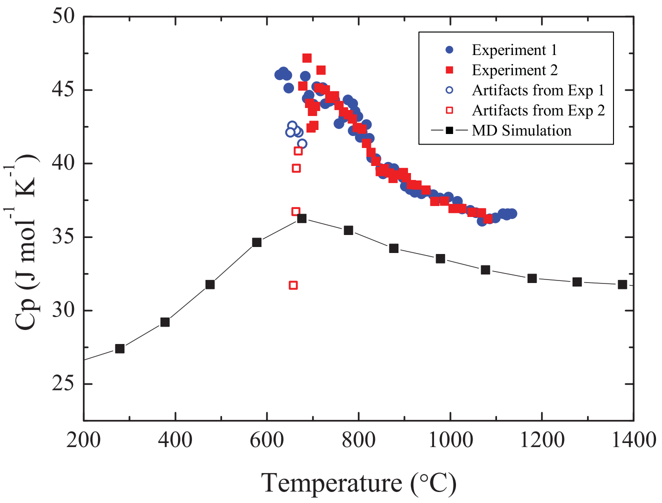

FIG. 3. (Color online) A quantitative comparison of $C_p(T)$ from experiments and MD simulations. The values measured experimentally are systematically greater than those from MD simulations. The last five data points from experiment 1 (hollow blue circles) and four data points from experiment 2 (hollow red squares) near the same temperatures may be artifacts resulting from an automatic gain change in the pyrometer used to measure temperature.

HG suggest. A recent reexamination by us of that data set revealed that an automatic gain change had occurred in the pyrometer at low temperature, which was not noticed earlier. This likely influenced the determination of $C_p(T)$ for the four lowest-temperature data points (indicated by the hollow red squares in Fig. 3) from experiment 2 and the five data points around the same temperature (hollow blue circles) from experiment 1. If these data points are ignored, the two data sets shown in the original paper[1] and here in Fig. 3 are equivalent; however, instead of a maximum, one observes a plateau, for both constant and temperature-dependent emissivities (Fig. 1). It should be emphasized, however, that the sudden increase in $C_p(T)$ and the plateau at lower temperature are not experimental artifacts (see the earlier discussion of emissivity), nor, as discussed earlier (Fig. 1), are they removed if a temperature-dependent emissivity is used. These features were extracted from pyrometry data for temperatures that were far above and below that where the automatic gain change occurred.

HG have raised valid concerns about an ambiguity in our comparison between the experimental and MD results in the original paper. As previously discussed, we never meant to imply that the measured behavior of $C_p(T)$ near 700 °C indicates a glass transition; this temperature is far above the calorimetric glass transition (380 °C). However, the decrease in $C_p(T)$ at lower temperatures in the MD results *is* associated with structural arrest. This makes comparison between the MD simulation and the experimental data problematic for the lowest temperatures. However, they are in good qualitative agreement at high temperatures and are consistent with the rapid chemical and topological ordering in the liquid that is inferred from the experimental scattering data. As shown in Fig. 7 in Ref. 1, the MD predictions of the greater rate of increase in $C_p(T)$ followed by the plateau are associated with the development of icosahedral order, in agreement with the results from RMC fits to the experimental data.

To aid further interpretation of the MD results, Mendelev (henceforth referred to as MIM) provided[36] data from his own calculations using methods described elsewhere[37] for two potentials, including the one that we used for the MD simulation in our original publication. The results of his calculations are essentially identical to ours above about 700 °C, when the same potential is used. In contrast to our methods, MIM equilibrated the system at each temperature during cooling, resulting in a sharper decrease in the heat capacity[37] (a "glass transition") when compared to the broad peak observed from our methods. It is well known that the behavior in the regime of the glass transition is highly dependent on cooling rate and cooling protocols,[38,39] and therefore the heat capacity in the lower-temperature regime is expected to change accordingly. This somewhat accounts for the difference between our MD results and those of MIM.[37] Generally, a slower cooling rate appears to produce a somewhat lower final energy and to achieve "arrest" at a lower temperature. Thus, it appears that MIM's protocol effectively achieves a slower cooling rate. Qualitatively, however, the results are similar: a peak in the heat capacity with a corresponding change in structure. Other results[4] also predicts a temperature region where the energy decreases rapidly during cooling, equivalent to a peak in the heat capacity.

HG also present a plausible explanation for the inconsistency that we noted between the observed volume fractions of the phases that formed on crystallization of the Cu-Zr liquids and what might be expected from the equilibrium phase diagram. Theirs is an interesting suggestion; however, since those data were presented as additional information and were not central to the theme of the paper, this point does not warrant further discussion here

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