Splitting up entropy into vibrational and configurational contributions in bulk metallic glasses: A thermodynamic approach

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In the present letter, we applied an efficient methodology to separate vibrational and configurational entropies in bulk metallic glasses by means of molecular dynamics simulation based on a combination of non-equilibrium adiabatic switching and reversible scaling methods. This approach involves calculating the vibrational free energy using the Einstein crystal as a reference for the solid phase and the recently proposed Uhlenbeck-Ford model for the fluid phase. This methodology has the advantage that it does not require a crystalline solid phase for separating the entropies. Therefore, in principle, it is applicable to any material, regardless of it having a crystalline phase or not. In this work, we separate the vibrational and configurational entropies of the binary Cu50Zr50 bulk metallic glass at zero external pressure. We find that the results are in quite reasonable agreement with recent experimental work by H. L. Smith et al. (Nature Physics 13, 900 (2017)) for the same binary metallic alloy. Moreover, the results indicate that the excess entropy of the glass with respect to the single crystal CuZr2 contains a slight contribution from the vibrational entropy.

The excess of entropy in glass-forming liquids with relation to crystalline phase is a phenomenon studied since early 1900’s. It started with the measurements of caloric properties of glass-forming substances done by Nernst in order to verify whether or not the third law of thermodynamics was applicable to all forms of condensed matter[1], that was followed by the publication in 1926 by Simon and Lange of their results about finite values of entropy for \( T = 0 \) K in glasses of glycerol and silica[2]. Soon after, similar results were reported in ethanol[3] and in the following years studies of excess entropy in glasses were extended to organic compounds[4–6], ionic melts, metallic alloys[7] and so on. Furthermore, Langer and Sethna showed that the excess of entropy usually calculated during heating (cooling) from the specific heat only provides an upper (lower) bound for the entropy[8]. Thus, at present, all known experimental results indicate that in the glass state the entropy is frozen-in in one almost constant value.

In order to explain this phenomenon Gibbs and DiMarzio[9] proposed for the first time a theoretical description based on a lattice polymer model, in which below the so-called glass transition temperature \( T_g \) the liquid is frozen-in in a single configuration and unable to explore other configurations. This idea lead to potential energy landscape description (PEL) articulated originally by Goldstein[10] as a topographic viewpoint of condensed phases and later formalized by Stilliger and Debenedetti[11]. In the framework of PEL it is possible to separate the entropy, at low temperatures, in two contributions. One part which is configurational, arising from the exploration of different basins, and other which is vibrational, originating from thermal motions intrabasin[12 13]. In the Gibbs-DiMarzio description there are not significant changes in the intrabasin vibration spectrum assuming that the excess of entropy in glasses is entirely configurational. Notwithstanding, in Goldstein’s viewpoint the excess of entropy has contributions from atomic and molecular vibrations. In this description, the excess of entropy decreases linearly due to the linear dependence of the temperature from the vibrational part, while the frozen-in configurational entropy remains constant below \( T_g \).

In this letter, we apply an efficient methodology based in non-equilibrium methods to separate the vibrational and configurational entropy in the binary Cu50Zr50 Bulk Metallic Glass (BMG) by means of molecular dynamics simulations. Even though, in principle, this methodology is applicable to any material, we choose the aforementioned metallic alloy because its properties are well known and reported in several experimental and theoretical studies[14–17]. Recently, the vibrational entropy contribution of Cu50Zr50 was obtained experimentally using direct \( in situ \) measurements of the vibrational spectra allowing, for the first time, to separate vibrational and configurational contributions of entropy in BMGs[18]. The authors in Ref. [18] obtained the vibrational entropy through density of states, \( g(E) \), which is rigorously valid to account for harmonic or quasiharmonic effects. Here, on the other hand, we employ a purely thermodynamic methodology to obtain the entropy from direct calculation of the free energy in the solid and liquid phases. This methodology offers two major advantages. First, all the anharmonic effects are accounted for during the calculation, and second, it is applicable to any material regardless of it having a crystalline phase or not. This is a desirable feature since most part of BMGs are composed by three or more elements with no crystalline stable phase.

Entropy, as well as free energy, are thermal variables, i.e., they depend on the entire accessible volume in the phase space. Thus, the calculations of these variables require special methods. In particular, for atomistic sim-
tions, several methods are available to obtain the free energies. In this work we used the adiabatic switching (AS) and reversible scaling (RS) methods, both based on thermodynamic integration, which allows one to compute excess free energy of the system of interest relative to a reference system for which the absolute free energy is already known. The RS method was implemented through molecular dynamics simulations carried out in the NPT ensemble, while the AS method used simulations in the NVT ensemble. Simulation cells containing 4000 atoms with periodic boundary conditions were employed to avoid surface effects.

In order to obtain the absolute free energy of the binary Cu$_{50}$Zr$_{50}$ metallic alloy through the AS method, we used the widely molecular dynamics code LAMMPS for the computer simulations with an EAM potential of Cu and Zr given in Ref. [24], and two reference systems, a collection of harmonic oscillators or the Einstein crystal (EC) and the Uhlenbeck-Ford model (UFM) (UFM), for solid and liquid phases, respectively.

Once the absolute free energies of the reference systems are obtained through the AS method, we use these values as references to calculate the free energies of the systems of interest in a wide range of temperatures using the RS method. This method provides an accurate estimation of the free energy, including all anharmonic effects. The deduction of the RS equation can be found in several references [21, 22, 23]. Here, we only present the final result,

$$ G(T) = \frac{G^0(T_0)}{\lambda} + \frac{3}{2} N k_B T_0 \ln \lambda + \frac{W(\lambda)}{\lambda}, \quad (1) $$

where $\lambda$ is a scaling parameter defined as: $\lambda = T_0/T$, $G^0(T_0)$ is the reference absolute free energy obtained by the AS method, and $W$ is the external work done as the scaling factor lambda is changed from 1 to $T_0/T$. This work is estimated as

$$ W = \int_1^{\lambda_f} \frac{d\lambda}{dt} U_{EAM}(\Gamma(t))dt, \quad (2) $$

where $\Gamma(t)$ is the vector in the phase space containing the information of all coordinates and momenta as a function of time. Thus, using (1), the absolute free energy is obtained from $T_0$ to a final temperature $T (= T_0/\lambda_f)$. Since the work done is calculated dynamically, a systematic error is generated during the process and therefore a measure of how far from the equilibrium the system configurations are during the calculation. However, if the switching process is performed slowly enough, such that the linear response is valid, the quasi-static work is extracted from that obtained dynamically in Eq. (2) [23]. This methodology is similar to that recently proposed by Berthier, Ozawa, and Scalliet [21], however, its computational cost is considerably lower than that of Ref. [30], since it does not require several equilibrium simulations.

Fig. 1a depicts the absolute free energy as a function of temperature for the binary Cu$_{50}$Zr$_{50}$ alloy of the glass and liquid states. It should be noted that the reference systems are only used to determine the reference free energies at low temperature ($G^0_{FL}$, for the solid at $T = 300$ K) and high temperature ($G^0_{UF}$, for the liquid at $T = 1800$ K). For details of how to perform AS-RS simulations see Refs. [32] and [33] for the solid and liquid phases, respectively. The value of $G^0_{UF}$ obtained for the liquid state at 1800K coincides well with the one previously reported in references [33, 34] for the same percentage of Cu and Zr. On the other hand, we are not aware of previous calculations of $G_{FL}$ for this alloy, nonetheless, it is well known that the Cu$_{50}$Zr$_{50}$ alloy crystallizes to B2 structure when it is cooled slowly enough. Therefore, in Fig. 1b we present the calculation of $G^0_{FL}$ and the melting point obtained using the RS method. The agreement between the results for B2 presented here and those computed in ref [31] is excellent. The crossing between the free energy curves for the crystal and the liquid phases gives the thermodynamic melting point, which was found to be approximately 1108 K, this value differs from the experimental melting point (1210 K) in about 100 K. This difference is due to the fact that the melting temperature is extremely sensitive to small changes in the free energy. All other calculations using empirical potential, analytical and also ab initio procedures provide the melting point with a relative error in relation with the experiment of approximately 8%.
The entropy is obtained through the numerical computation of $S = -\left(\partial G/\partial T\right)$. The entropy of the glass is composed by two contributions, vibrational and configurational. In the liquid phase the entropy, $S_{FL}$ contains both contributions. Since the glass is a solid, for $T < T_g$, we can compute its vibrational entropy, $S_{vib} = S_{FL}$, from the vibrational free energy $G_{FL}$. Thus, for temperatures lower than $T_g$, the difference $\Delta S = S_{UF} - S_{FL}$ represents the configurational contribution to the entropy, $S_{con}$.

For temperatures greater than $T_g$, $\Delta S \neq S_{con}$ because the glass turns into a liquid and $S_{FL}$ gains a configurational contribution. The Savitzky-Golay smoothing filter, performing a polynomial regression of third order, was used for noise reduction in the results of the configurational entropy. In Fig 2 we reveal the behavior of $S_{UF}$, $S_{FL}$ and $\Delta S$ for binary Cu$_{50}$Zr$_{50}$.

The vibrational entropy decreases with decreasing the temperature approximately at the same rate as that the liquid. The difference of the entropies, on the other hand, which is the configurational entropy of the liquid at the moment of the glass transition, remains frozen-in in the structure of the glass. These are the reasons for $\Delta S$ to be approximately constant for temperatures below of the glass transition.

The behavior depicted in Fig 2 can be understood through potential energy landscape (PEL), because the configurational entropy is related with the density of basins accessible at a given energy. Thus, the configurational entropy increases with increasing temperature as additional basins become accessible to the system with increasing temperature. Moreover, for temperatures below $T_g$ the system is trapped in a specific basin leading $\Delta S$ to be frozen in at a constant value when the system becomes a glass.

In a recent work, Smith et al.\cite{18}, experimentally separated the configurational and vibrational entropies of the same alloy using in-situ neutron diffraction and differential scanning calorimetry.

An overall picture of the vibrational and configurational entropies of the glass compared with the experiment can be viewed in TABLE I. There is a quite reasonable agreement between our results and the experimental findings, in particular if one takes into account that the configurational entropy in this case is a small quantity, resulting from the difference between two numerically similar quantities, namely, $S_{UL}$ and $S_{FL}$.

The findings of Smith et al. were obtained by determining the vibrational entropy of the glass and the crystal of the alloy in a range of temperatures of about 100 K below $T_g$. They found that the vibrational entropy of the glass is almost equal to its crystalline counterpart for that interval of temperatures, concluding that the excess entropy, i.e., the difference of entropy between crystal and liquid phases for temperatures below $T_g$, is entirely configurational. In order to compare our results with Smith’s experimental work, we calculate the vibrational entropy of the crystalline phase. However, below 988 K the B2 structure decompose into a mixture of two crystalline phases Cu$_{110}$Zr$_7$ and CuZr$_2$. Since we are not aware of the exact amount of each phase we analyzed the behavior of these phases separately. The results are depicted in Fig. 3a.

These results are better understood within the PEL framework. The glass state is the result of the system being "trapped" in a local minimum of energy landscape, as a consequence of fast cooling. In RS simulations, we are actually increasing the temperature of the system and, therefore, the energy. Thus, the vibrational entropy has a similar behavior below $T_g$. However, above $T_g$ the system in the glass state has enough energy to scape of the local minimum and access other states, i.e., the glass de-vitrifies. The crystals on the other hand, are held at absolute minima, since at $T_g$ the energy is not enough to allow them to scape from absolute minimum.

Fig. 3a shows that at $T_g$ the vibrational entropy of the crystals differ from that of the glass by a small amount, in contrast to the findings of Smith et al. A possible explanation for this discrepancy is that in their case, the crystal is a mixture of crystalline phases and there could be significant anharmonic contributions to the vibrational entropy coming from the interfaces between the two crys-
a function of temperature. For temperatures above \( T_g \), the glass turns to a liquid and the entropy \( S_{FL} \) is no longer only vibrational, containing also a configurational part. (b) The excess entropy as a function of temperature. Since the vibrational contributions to the entropy without comparing the results for the glass with those for a crystal. This advantage is very important in this case, since in the experiment the glass crystallizes into a mixture of crystalline structures, mostly \( \text{Cu}_{10}\text{Zr}_7 \) and \( \text{CuZr}_2 \), whose microstructure is not accessible, preventing a direct comparison of our results with the experiment. Nevertheless, in order to further investigate these properties, we computed the vibrational entropies of the two crystalline structures separately. Our findings show that for temperatures about 300 K, the vibrational entropy of the glass is very close to those of the two crystalline structures, however, as temperature approaches \( T_g \), the vibrational entropy of the glass increases slightly more rapidly with temperature than the vibrational entropy of the single crystals, because of anharmonic effects in the glass. Our results for the excess entropy of the glass with respect to the single crystal structures show that, because of the slight difference between the vibrational entropies of glass and crystal, the excess entropy increases linearly with temperature for temperatures below \( T_g \), this is accord with Goldstein’s description of excess entropy \([10]\), instead of the that of Gibbs and de Marzio \([9]\) observed in the experiment \([18]\). This discrepancy is possibly due to anharmonic effects in the crystal used as reference in the experiment, which is a mixture of crystalline structures.

In summary, we have separated the vibrational and configurational contributions to the entropy of the \( \text{Cu}_{50}\text{Zr}_{50} \) metallic glass through computer simulations. We employed in our calculations a robust methodology, whose qualities are evidenced by the good agreement between the results of our simulations and experimental available data \([9,18]\) for the vibrational and configurational entropies of this metallic glass. The main advantage of this methodology is that one can separate the two contributions to the entropy without comparing the results for the glass with those for a crystal. This advantage is very important in this case, since in the experiment the glass crystallizes into a mixture of crystalline structures, mostly \( \text{Cu}_{10}\text{Zr}_7 \) and \( \text{CuZr}_2 \), whose microstructure is not accessible, preventing a direct comparison of our results with the experiment. Nevertheless, in order to further investigate these properties, we computed the vibrational entropies of the two crystalline structures separately. Our findings show that for temperatures about 300 K, the vibrational entropy of the glass is very close to those of the two crystalline structures, however, as temperature approaches \( T_g \), the vibrational entropy of the glass increases slightly more rapidly with temperature than the vibrational entropy of the single crystals, because of anharmonic effects in the glass. Our results for the excess entropy of the glass with respect to the single crystal structures show that, because of the slight difference between the vibrational entropies of glass and crystal, the excess entropy increases linearly with temperature for temperatures below \( T_g \), this is accord with Goldstein’s description of excess entropy \([10]\), instead of the that of Gibbs and de Marzio \([9]\) observed in the experiment \([18]\). This discrepancy is possibly due to anharmonic effects in the crystal used as reference in the experiment, which is a mixture of crystalline structures.

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