



# A new method for measuring the thermodynamic properties of undercooled liquid and amorphous Cu–Zr alloys

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## Abstract

A new method for the experimental determination of the temperature-dependent heat capacity is presented here. The value of this new method lies principally in its applicability to unstable systems, where time-dependent relaxation processes limit the utility of conventional stepwise methods that employ a series of isothermal holding periods. The method is demonstrated for two glass-forming alloys ( $\text{Cu}_{50}\text{Zr}_{50}$  and  $\text{Cu}_{64.5}\text{Zr}_{35.5}$ ), using differential scanning calorimetry (DSC) measurements over a (low) temperature regime including stable, metastable and unstable states (crystalline, glass and undercooled liquid). For this specific analysis, the glassy material is heated using several different rates, each resulting in a different transformation temperature. After characterization of the final states, analysis of the DSC traces yields the requisite transition enthalpies, enabling determination of the heat capacities, based on common reference states. © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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## 1. Introduction

Metallic glasses have great potential importance, owing both to the remarkable properties exhibited by non-crystalline phases as well as to the avenues that a glass may provide toward achieving novel multiscale structures and metastable crystalline phases. To assess glass/crystal competition and to exploit such far-from-equilibrium transformation pathways, the thermodynamic and kinetic properties of the undercooled liquid phase must be quantified. Atomistic simulations [1–4] and advanced scattering studies [5–7] can provide new insights into the pair and many-body correlations that give rise to short- and medium-range topological and chemical ordering in undercooled metallic liquids and glasses. However, the need clearly exists for comprehensive solution-based thermodynamic treatments that predict bulk properties, describe relevant energy landscapes

and facilitate the modeling of nanoscale/mesoscale dynamics under far-from-equilibrium conditions. To this end, comprehensive thermodynamic descriptions of the undercooled liquid are essential, but, given the unstable nature of an undercooled metallic liquid, the prospects for measuring its basic thermodynamic properties (heat capacity, molar volume, etc.) using standard methods are rather limited. Levitation techniques have enabled heat capacity estimations for slightly undercooled liquids [8–13], but such estimates are sensitive to the emissivity of the liquid, which is not always known and is often assumed or estimated. Various calorimetric techniques have been used to determine the heat capacity of deeply undercooled liquids [14–18], but melt instability and uncertainties in instrument or “baseline” thermal losses present significant challenges to performing accurate measurements. We examine the problem generally here, and then present a method that has particular applicability to the measurement of thermodynamic properties in temperature regimes where relaxation transitions occur at appreciable rates and cannot be neglected.

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We consider a material specimen contained in an inert ampoule, where no chemical reactions or phase transformations occur except for those exhibited by the specimen itself. The heat required to change the system temperature by a differential increment  $dT$  is given by:

$$\delta q = \delta q_S + \delta q_A + \delta q_L, \quad (1)$$

where the individual terms denote the heat entering the specimen, the heat entering the ampoule, and the inherent heat loss associated with the instrument design and the irreversible nature of the heat transfer process. Accordingly, for any instrument configuration, there is particular heat flux required to exactly offset  $\delta q_L$  and simply maintain the specimen and ampoule at a constant temperature. Moreover, this value depends generally on system temperature and many other experimental parameters, e.g. the mass and the shape of the specimen and ampoule, and the state of the instrument itself. While these cannot generally be predicted, they can, in some cases, be quantified as a part of the experimental procedure. Indeed, such quantification is required for accurate determination of  $\delta q_S$  for a given temperature ( $T$ ), and the associated effective heat capacity,  $C_P^{eff}(T) \equiv [\delta q_S(T)/dT]/m$ , where  $m$  is the mass of the specimen. For a specimen containing  $j$  phases at a constant pressure ( $P$ ), we have:

$$\begin{aligned} C_P^{eff} &= \left( \frac{dh_S(T, f_1, f_2, \dots, f_j)}{dT} \right)_P \\ &= \left( \frac{\partial h_S}{\partial T} \right)_{P, f_1, f_2, \dots, f_j} + \sum_{\alpha=1}^j \left( \frac{\partial h_S}{\partial f_\alpha} \right)_{P, T, f_{\beta \neq \alpha}} \frac{df_\alpha}{dT} \\ &= \sum_{\alpha=1}^j \left[ f_\alpha \left( \frac{\partial h_\alpha}{\partial T} \right)_P + h_\alpha \frac{df_\alpha}{dT} \right] \\ &= \sum_{\alpha=1}^j \left( f_\alpha C_P^\alpha + h_\alpha \frac{df_\alpha}{dT} \right), \end{aligned} \quad (2)$$

where  $h_S = \sum_{\alpha=1}^j f_\alpha h_\alpha$ ,  $f_\alpha$ ,  $h_\alpha$  and  $C_P^\alpha$  are the mass fraction, the specific enthalpy and the specific heat capacity of phase  $\alpha$ , respectively. For any path from  $T_1$  to  $T_2$  employing a constant heating or cooling rate,  $\dot{T}$ , the required heat flow,  $\dot{q}$ , can be written as:

$$\dot{q} = \dot{q}_S + \dot{q}_A + \dot{q}_L = m C_P^{eff} \dot{T} + \dot{q}_A + \dot{q}_L. \quad (3)$$

A typical strategy is to determine the sum  $\dot{q}_A + \dot{q}_L$  by direct measurement. For example, the empty-ampoule response,  $\dot{q}_A$ , can be independently measured for a given path by subjecting the ampoule itself to the same heating profile that is applied to the ampoule–specimen system. The baseline loss flux,  $\dot{q}_L$ , can be measured for any specific temperature using an isothermal hold, provided that no physical or chemical reactions are occurring with time at the isothermal hold temperature. This practice can be incorporated with a non-isothermal “scan” by implementing multiple isothermal arrests at selected temperatures within the scan and then using linear (or other) interpolation to describe the behavior between arrest temperatures.

This method is reasonable if no reaction or transformation is occurring during the isothermal holding periods and if the difference between arrest temperatures is small. For a scan over a small temperature range, only endpoint isothermal arrests may be necessary [19]. However, if measurements over a large temperature range are required, interpolation from endpoints only is not sufficient to characterize  $\dot{q}_L(T)$ . In this case, a long heating or cooling path can be interrupted with many isothermal holding periods, providing measurements of many points along the path. Thus, a more accurate baseline loss function can be fit over the temperature range or, at worst, linear segments between measured points can be used. This is known as the stepwise correction method [19,20]. Because losses can be quantified directly using the specimen and ampoule configuration at many points along the path, errors associated with poorly quantified baseline losses can be significantly reduced. However, the limitation remains that this method is not appropriate if any reactions or transformations are occurring during the isothermal holding periods. Regarding metastable phases (crystalline or amorphous), the method is best applied to the low-temperature regime, where no discernible relaxation or crystallization mechanisms are operative. Accordingly, while successful application of the stepwise method to low-temperature glasses (significantly below the glass transition temperature  $T_g$ ) have been reported [16,21], direct measurements of  $C_P(T)$  in undercooled metallic liquids remains a challenge.

In this work, we develop a new “Q-method” for accurate experimental determination of  $C_P$  in an undercooled glass-forming metallic liquid. The method is demonstrated for alloy compositions of  $\text{Cu}_{50}\text{Zr}_{50}$  and  $\text{Cu}_{64.5}\text{Zr}_{35.5}$  for temperatures above the glass transition temperature ( $T_g$ ) and much below the respective congruent melting temperature ( $T_m$ ) or liquidus temperature ( $T_L$ ). Using DSC measurements, we compare directly the Q-method to a stepwise measurement approach for these alloys.

As an important metallic glass system with good glass-forming ability over a large composition range, the Cu–Zr system has been widely studied both experimentally and theoretically. There are many different thermodynamic descriptions [22–27] available for the Cu–Zr binary system. These are generally consistent with respect to the high-temperature liquid, but substantial differences appear at lower temperatures. For example, the mixing enthalpies of liquid at 1480 K [28,29] were fitted by almost all modeling work, and the calculated values from different databases [23–27] are in good agreement with each other. The sub-regular solution model was adopted by Saunders [22], Zeng and Hamalainen [23] and Wang et al. [25] for the liquid phase, resulting in temperature-independent mixing enthalpies. The concept of association was used by Zaitsev et al. [24] and Zhou and Napolitano [27] to describe the temperature-sensitive properties of the liquid phase. Their calculated mixing enthalpies at 298 K are significantly lower than those from the sub-regular solution model [22,23,25]. Zaitsev et al. [24] introduced two associates

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