

## Multiple melting temperatures in glass-forming melts Robert Tournier, Michael I Ojovan

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### Article Multiple melting temperatures in glass-forming melts

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Abstract: All materials are vitrified by fast quenching even monoatomic substances. Second melting 10 temperatures accompanied by weak exothermic or endothermic heat are often observed at Tn+ after 11 remelting them above the equilibrium thermodynamic melting transition at Tm. These temperatures 12  $T_{n+}$  are due to the breaking of bonds (configurons) or antibonds depending on the thermal history 13 which is explained by using a non-classical nucleation equation. Their multiple existence in mono-14 atomic elements is now demonstrated by molecular dynamics simulations and still predicted. Pro-15 posed equations show that crystallization enthalpy is reduced at the temperature  $T_x$  due to new 16 vitrification of non-crystallized parts and their melting at Tn+. These glassy parts being equal above 17  $T_x$  to singular values or to their sum are melted at various temperatures  $T_{n+}$  and attains 100% in 18 Cu<sub>46</sub>Zr<sub>46</sub>Als and 86.7% in bismuth. These first-order transitions at Tn+ are either reversible or irre-19 versible depending on the formation of superatoms either solid or liquid. 20

**Keywords:** metallic glasses; melting temperatures; liquid-liquid transitions, chemical bonds; vitrification, crystallization, first order transitions

#### 1. Introduction

Liquid-liquid phase transitions occur in glass-forming melts below and above T<sub>m</sub>, the 25 equilibrium thermodynamic melting transition of crystals. These transitions are driven by 26 density separation of two liquid states existing in all supercooled and overheated materi-27 als including pure elements in which two liquid phases of the same composition coexist 28 [1-15]. Denser glassy phases are built by vapor deposition below the glass transition tem-29 perature T<sub>g</sub> leading to higher glass transition temperatures and first-order transitions to-30 ward liquid states [16-19]. Glacial phases with higher values of Tg result from first-order 31 transitions between  $T_g$  and  $T_m$  [20-25]. Denser phases called G-Phases are obtained in liq-32 uid elements by numerical simulations at very high heating rates, leading to second melt-33 ing temperatures far above Tm [26-29]. Glass-forming melts undergo liquid-liquid transi-34 tions with endothermic or exothermic latent heats at nucleation temperatures  $T_{n+}$  higher 35 than  $T_m$  [30-36]. First-order transitions are observed at temperatures  $T_{n+}$  above  $T_m$  with 36 nuclear magnetic resonance by cooling a homogeneous liquid, followed by homogeneous 37 nucleation of growth nuclei below Tn+ leading to melt crystallization [37,38]. Multiple liq-38 uid-liquid transitions were observed at low heating rates in bismuth [39.40] and glass-39 forming melts of Cu-Zr-Al [41]. It is the purpose of this publication to relate the various 40glass phases to melting transitions above Tm following proposals of H. Tanaka [15,42]. 41

Liquid–liquid structure transition plays an important role in the final microstructure 42 and the properties of solid alloys [43]. Solidifying  $Bi_2Te_3$  alloys after melting above  $T_{n+}$  43 followed by various cooling rates refined the microstructure and increased the hardness 44 with cooling rate [44,45]. Solidifying magnetic melts after overheating below  $T_{n+}$  in high magnetic fields built textured congruent and non-congruent substances [46], crystals or 46

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**Copyright:** © 2022 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/license s/by/4.0/). even permanent magnets with particle easy-magnetization axis oriented along the mag-<br/>netic field due to the presence of growth nuclei in melts above  $T_m$  [47]. The classical nu-<br/>cleation equation cannot explain such nucleation phenomena [48,49].47484949

A non-classical nucleation equation involving two liquid states was built by adding 50 an enthalpy contribution  $\varepsilon H_m$ , with  $\varepsilon$  depending on  $\theta^2 = (T-T_m)^2/T_m^2$  and being a fraction of 51 the crystal melting heat  $H_m$  to complete the Gibbs free energy of nuclei above and below 52  $T_m$  [50]. The undercooling rate of liquid elements were predicted leading to an average 53 minimum value of  $\varepsilon = 0.217$  for  $\theta = 0$  due to the Lindemann coefficient at T<sub>m</sub> [51]. The 54 nucleation equations of liquids 1 and 2 were used to successfully predict the specific heat 55 jump at the glass transition temperature  $T_{g}$ , the VFT temperatures of fragile liquids above 56  $T_m/3$  [52-54] and the first temperature  $T_{n+}$  [55]. The nature of surviving entities are super-57 clusters (superatoms), melted by liquid homogeneous nucleation instead of surface melt-58 ing [56,57]. 59

The enthalpy and entropy variations of supercooled water at  $T_{LL}$ = 228.5 K [58,59] during the first cooling were predicted [60]. The formation below  $T_g$  of a glacial phase called Phase 3, having an enthalpy equal to the difference between those of liquids 1 and 2, explained why the transition at  $T_{LL}$  disappears during the first heating. The theoretical firstorder transitions of Phase 3 under pressure reproduced those found by Speedy and Angell [61]. The phase diagram of water confined into carbon nanotubes was similar to that predicted by numerical simulations [62,63].

The thermodynamic properties of glass-forming melts are easy to predict when Tg 67 and  $T_m$  are known. The singular enthalpy values of Phase 3 are zero and those calculated 68 at T= T<sub>m</sub>, T<sub>g</sub>, T<sub>om</sub>, the VFT temperatures of liquids 1 and 2 and the first temperature T<sub>n+</sub>. 69 The nucleation equations of glacial phases used these singular enthalpies as latent heats 70 to fix the entropy-driven transition temperatures [64,65] of triphenyl phosphite [22,25], D-71 mannitol [24], n-butanol [23,66,67], and Zr41.2Ti138Cu12.5Ni10Be22.5 [35,36]. The stable and ul-72 trastable glasses formed by vapor deposition had enthalpies equal to singular values and 73 their transition temperatures at T<sub>g</sub> are driven by them. Other melts had also enthalpy-74 driven transitions such as Ti<sub>34</sub>Zr<sub>11</sub>Cu<sub>47</sub> Ni<sub>8</sub> [68], and Co<sub>81.5</sub>B<sub>18.5</sub> [43] in agreement with the 75 predictions [65]. A critical supercooling and overheating rate  $\Delta T/T_m = 0.198$  of liquid ele-76 ments was predicted in agreement with experiments on Sn droplets [69]. 77

Phase 3 formation has for origin a second-order phase transition associated with critical exponents due to bonds breaking (configurons formation) when a glass is heated through  $T_g$  [70-75]. The Gibbs free energy of configurons disappears at  $T_{n+}$  instead of  $T_g$ [62,76,77]. The debate about the absence and the presence of phase transition at  $T_g$  is probably solved by these considerations.

The non-classical nucleation model predicted the G-phase formation in liquid elements via first-order transitions, and the second melting temperatures observed by molecular dynamics simulations at very high heating rates [78,79].

The question of their observation at low heating rates was raised, considering that the crystallization enthalpy of these elements would be reduced and recovered via liquid-liquid transitions occurring above T<sub>m</sub>. The singular values of the latent heats in all glass-forming melts could correspond to percolation thresholds at various temperatures.

The coexistence of glassy phases with crystals is known and viewed as being due to phase separation after annealing near T<sub>x</sub>, the crystallization temperature of glass-forming melts. This coexistence could result in fact from the presence of a glassy fraction in nano-crystallized materials having a glass transition temperature T<sub>g</sub> higher than T<sub>m</sub> as already shown for liquid elements [79].

This paper is devoted to the second vitrification of melt fractions at temperatures  $T_x$ 95coexisting with crystals formation and predictions of multiple melting temperatures  $T_{n+}$ 96of this glassy fraction above Tm from singular enthalpies of glass-forming melts.97

#### 2. The homogenous nucleation of two glassy states

2.1. The bulk glassy state below  $T_g$ 

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The Gibbs free energy change for a nucleus formation in a melt is given by (1) [(50)]: 100

$$\Delta G_{ls} = (\theta - \varepsilon_{ls}) \Delta H_m / V_m \times 4\pi R^3 / 3 + 4\pi R^2 \sigma_{ls}, \tag{1}$$

where R is the nucleus radius and following Turnbull [48],  $\sigma_{ls}$  its surface energy, given by (2),  $\theta$  the reduced temperature (T-T<sub>m</sub>)/T<sub>m</sub>,  $\Delta$ H<sub>m</sub> the melting enthalpy at T<sub>m</sub>, and V<sub>m</sub> the molar volume:

$$\sigma_{ls} (V_{\rm m}/N_{\rm A})^{-1/3} = \alpha_{\rm ls} \Delta H_{\rm m}/V_{\rm m}, \tag{2}$$

A complementary enthalpy  $\epsilon_{ls} \times \Delta H_m/V_m$  is introduced, authorizing the presence of 104 growth nuclei above and below  $T_m$  with  $\epsilon_{ls}$  being positive or negative above  $T_m$  depending 105 on its increase or decrease with  $\theta$ . In previous works,  $\epsilon_{ls}$  was only positive [50,52,54,80]. 106 The discovery of positive or negative enthalpy above  $T_m$  related to the presence of antibonds or bonds sets this new rule [77]. The classical nucleation equation is obtained for 108  $\epsilon_{ls}= 0$  and leads to a homogeneous liquid above  $T_m$ . 109

The critical thermally activated energy barrier  $\Delta G^*_{1s}/k_BT$  is calculated in (3) assuming 110  $d\epsilon_{1s}/dR = 0$ : 111

$$\frac{\Delta G_{ls}^*}{k_B T} = \frac{16\pi\Delta S_m \alpha_{ls}^3}{3N_A k_B (1+\theta)(\theta-\varepsilon_{ls})^{2'}}$$
(3)

where  $\Delta S_m$  is the melting entropy [48,50,54,81]. This critical parameter is no longer infinite 112 at the melting temperature  $T_m$  because  $\varepsilon_{1s}$  is not equal to zero. This event now occurs above 113  $T_m$  for  $\theta = \varepsilon_{1s}$ . The nucleation rate J = K<sub>v</sub> exp( $-\Delta G^*_{1s}/k_B T$ ) is equal to 1 when (4) is respected: 114

$$\Delta G_{ls}^* / k_B T = \ln (K_v), \qquad (4)$$

The surface energy coefficient  $\alpha_{1s}$  in (2) is determined from (3,4) and equal to (5): 115

$$\alpha_{ls}^{3} = \frac{3N_{A}k_{B}\left(1+\theta\right)\left(\theta-\varepsilon_{ls}\right)^{2}}{16\pi\Delta S_{m}}\ln\left(K_{v}\right),$$
(5)

The nucleation temperatures  $\theta_{n-}$  and  $\theta_{n+}$  obtained for  $d\alpha_{1s}^3/d\theta = 0$  obey (6):

$$d\alpha_{ls}^{3}/d\theta \sim (\theta_{n+} - \varepsilon_{ls})(3\theta_{n-} + 2 - \varepsilon_{ls}) = 0,$$
(6)

There are two families of nucleation temperatures:  $\theta_{n-} = (\epsilon_{ls}-2)/3$  far below  $T_m$  and  $\theta_{n+} = 117$  $\epsilon_{ls}$  above  $T_m$ . In addition to the nucleation temperatures  $T_{n-}$  below  $T_m$ , the existence of a 118 homogenous nucleation temperature  $T_{n+}$  above  $T_m$  is confirmed by many experiments, observing the undercooling versus the overheating rates of liquid elements, and glass-forming melts [43,69,82-85]. This nucleation temperature has for consequence, the existence of 211 a second melting temperature  $T_{n+}$  of growth nuclei above  $T_m$  and of their homogeneous nucleation at temperatures weaker than  $\theta_{n+}$  as shown in several publications [30-39,86-89]. 123

The coefficient  $\epsilon_{ls}$  of the initial liquid state called liquid 1 is a quadratic function of  $\theta$  124 in (7) [50] for  $\epsilon_{ls} > 0$  above T<sub>m</sub> in (1): 125

$$\varepsilon_{\rm ls} = \varepsilon_{\rm ls0} (1 - \theta^2 / \theta_{\rm 0m}^2), \tag{7}$$

where  $\theta_{0m}$  is the Vogel-Fulcher-Tammann (VFT) reduced temperature leading to  $\epsilon_{ls} = 0$  for  $\theta = \theta_{0m}$ , and the VFT temperature T<sub>0m</sub> of many fragile liquids being equal to  $\approx 0.77$  Tg. This quasi-universal value is known for numerous fragile liquids including atactic polymers [90,91].

New liquid states are obtained for  $\theta = \theta_{n+} = \epsilon_{ls}$  and  $\theta = \theta_{n-} = (\epsilon_{ls}-2)/3$  where  $\epsilon_{ls}$  is given in (7). The reduced nucleation temperatures  $\theta_{n-}$  are solutions of the quadratic equation (8): 131

$$\varepsilon_{\rm ls0}\theta_{\rm n-}^2/\theta_{\rm 0m}^2 + 3\theta_{\rm n-} + 2 - \varepsilon_{\rm ls0} - \Delta\varepsilon = 0, \text{ or } \varepsilon_{\rm ls}(\theta = 0) = (3\theta_{\rm n-} + 2 - \Delta\varepsilon)/(1 - \frac{\theta_{\rm n-}^2}{\theta_{\rm 0m}^2})$$
(8)

where  $\Delta \epsilon$  is an enthalpy-coefficient change, which can induce a first-order transition [55]. 132

There is a minimum value of  $\varepsilon_{1s0}$  plotted as a function of  $\theta_{0m}$  using (8) for  $\Delta\varepsilon=0$  and 133  $\theta_{n-} = (\varepsilon_{1s}-2)/3$ , determining the relation (9) between  $\theta_{20m}$  and  $\varepsilon_{1s0}$  for which the two solutions 134 of (8) are equal in fragile liquids [52,53]. These values define the temperature where the 135 surface energy is minimum and  $\theta_{20m}$  and  $\varepsilon_{1s0}$  obey (9) and (10): 136

$$\theta_{0m}^2 = \frac{8}{9} \varepsilon_{ls0} - \frac{4}{9} \varepsilon_{ls0'}^2$$
(9)

$$\varepsilon_{\rm ls}(\theta = 0) = \varepsilon_{\rm ls0} = 1.5\theta_{\rm n-} + 2 = a\theta_{\rm g} + 2,$$
 (10)

Eq. (9) leads to  $T_{0m} = 0.769 \times T_g$  for a= 1 in agreement with many experimental values [52].

All melts and even liquid elements undergo, in addition, a bulk glass transition because another liquid state called liquid 2 exists characterized by an enthalpy coefficient  $\varepsilon_{gs}$  140 given by (11) inducing an enthalpy change from that of liquid 1 at the thermodynamic transition at  $\theta_{g}$  [53,54,80]: 142

$$\varepsilon_{\rm gs} = \varepsilon_{\rm gs0} (1 - \theta^2 / \theta_{\rm 0g}^2) - \Delta \varepsilon, \tag{11}$$

where  $\theta_{0g^2}$  and  $\varepsilon_{gs0}$  obey (12,13) for  $\varepsilon_{1s} > 0$  and  $\Delta \varepsilon$  is zero at the glass transition:

$$\theta_{0g}^2 = \frac{8}{9} \varepsilon_{gs0} - \frac{4}{9} \varepsilon_{gs0}^2, \tag{12}$$

$$\epsilon_{\rm gs}(\theta = 0) = \epsilon_{\rm gs0} = 1.5\theta_{\rm n-} + 2 = 1.5\theta_{\rm g} + 2,$$
 (13)

The reduced nucleation temperatures  $\theta_{n-}$  are solutions of the quadratic equation (14): 144

$$\varepsilon_{g0}\theta_{n-}^2/\theta_{0g}^2 + 3\theta_{n-} + 2 - \varepsilon_{gs0} - \Delta\varepsilon = 0, \text{ or } \varepsilon_{gs}(\theta = 0) = (3\theta_{n-} + 2 - \Delta\varepsilon)/(1 - \frac{\theta_{n-}^2}{\theta_{0g}^2})$$
(14)

where  $\Delta \epsilon$  is the enthalpy-coefficient change inducing a first-order transition [55,66]. Eqs (8) and (14) lead to the same nucleation temperature  $T_{n-} = T_g$  for the same coefficient  $\Delta \epsilon$  in fragile liquids. 147

#### 2.2. The glassy state of Phase 3 up to the melting temperature $T_{n+}$ above $T_m$ 148

The difference  $\Delta \varepsilon_{lg}$  in (15) between the coefficients  $\varepsilon_{ls}$  and  $\varepsilon_{gs}$  determines the Phase 3 149 and the configuron enthalpies when the quenched liquid has escaped crystallization 150 [58,59,76]: 151

$$\Delta \varepsilon_{\rm lg}(\theta) = \left[\varepsilon_{\rm ls} - \varepsilon_{\rm gs}\right] = \left[\varepsilon_{\rm ls0} - \varepsilon_{\rm gs0} - \Delta \varepsilon - \theta^2 \left(\frac{\varepsilon_{\rm ls0}}{\theta_{\rm 0m}^2} - \frac{\varepsilon_{\rm gs0}}{\theta_{\rm 0g}^2}\right)\right],\tag{15}$$

The assumption of a= 1 in (10) defining the value of  $T_{0m}$  in (9) is the unique value for 152 which the activation energies  $B_1RT/(T-T_{0m})$  and  $B_2RT/(T-T_{0g})$  of liquids 1 and 2 are equal at 153  $T_g$  leading to an activation energy equal to zero for Phase 3 [76]. 154

When the enthalpy coefficients  $\varepsilon_{ls}(\theta)$  and  $\varepsilon_{gs}(\theta)$  are negative in (1), the phase 3 enthalpy coefficient  $\Delta \varepsilon_{lg}(\theta)$  becomes equal to (16): 156

$$\Delta \varepsilon_{\rm lg}(\theta) = -\left[\varepsilon_{\rm ls} - \varepsilon_{\rm gs}\right] = -\left[\varepsilon_{\rm ls0} - \varepsilon_{\rm gs0} - \Delta \varepsilon - \theta^2 \left(\frac{\varepsilon_{\rm ls0}}{\theta_{\rm 0m}^2} - \frac{\varepsilon_{\rm gs0}}{\theta_{\rm 0g}^2}\right)\right], \quad (16)$$

It increases with  $\theta$  in (15) or decreases in (16) because of its dependence on the thermal history and disappears at T<sub>n+</sub>. Two reduced glass transition temperatures  $\theta_g$  and  $-\theta_g$  158 exist. Another analogous equation leading to  $\Delta \varepsilon_{lg}$  ( $\theta$ ) given in (16) can be determined 159 using the new coefficients  $\varepsilon_{ls0}$  and  $\varepsilon_{gs0}$  in (10,13) obtained by changing  $\theta_g$  in  $-\theta_g$  and  $\theta^2_{0m}$ , 160  $\theta^2_{0g}$  deduced from (9,12) using these new values of  $\varepsilon_{ls0}$  and  $\varepsilon_{gs0}$ . 161

These new considerations show the existence of a glassy state of a melt fraction disappearing at the virtual transition temperature  $T'_g = 2T_m - T_g$  governing the thermodynamics of all Phases 3 including those nucleated by first-order transitions. This phenomenon 164

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of double glass state occurs because all glass-forming melts heated from their glass state 165 are composites containing an ordered fraction of percolating bonds or antibonds (15 ± 1 % 166 minimum) and a homogeneous liquid (85 % maximum) [62,76,77]. The first glass transition 167 temperature, observed at  $T_g$  below  $T_m$  by heating, corresponds to the percolation of con-168 figurons in the bulk liquid while the second transition only due to Phase 3 disappears at 169  $T_{n+}$  far above  $T_m$ . The partial glass state is preserved up to the nucleation temperature  $\theta_{n+}$ = 170  $\Delta \epsilon_{lg}$  ( $\theta_{g}$ ) because the ordered fraction remains equal to the percolation threshold observed 171 at  $\theta_g$  below  $T_m$ . The melt transformations at  $\theta_{n+}$  are sharp and only observable below the 172 virtual glass transition occurring at  $\theta'_g = -\theta_g$ . Note that the two VFT temperatures above 173  $T_m$  corresponding to this virtual glass transition are also virtual because  $\theta^{2}_{0m}$  and  $\theta^{2}_{0g}$  are 174 negative in this case. 175

#### 3. Reduction of the crystallization enthalpy at the crystallization temperature T<sub>x</sub>

The enthalpy recovery during heating is endothermic at  $T_{n+}$  for bonds and exothermic177for antibonds breaking [77]. The total melting enthalpy H depends on the reduced temperature  $\theta_{n+}$  because this homogeneous nucleation temperature  $T_{n+}$  occurs above  $T_m$  with178the enthalpy change  $\Delta \varepsilon_{lg}$  ( $\theta_{n+}$ ) =  $\pm \theta_{n+}$  [1] for  $\theta_{n+} < -\theta_g$ .180

Heating from the glass state below Tg can induce, at the same time, a first-order tran-181 sition at  $T_{x_r}$  toward crystallization and nucleation of a new glassy state of Phase 3 with a 182 latent heat  $-\Delta \epsilon H_m$  and a new glass transition temperature  $T'_g = 2T_m - T_g$ . The reduced tem-183 perature  $\theta_x$  is given by Eq. (14) with  $\Delta \varepsilon$  equal to singular values of the enthalpy coefficient 184  $\Delta \epsilon_{lg}$  of Phase 3. These singular values are zero,  $\Delta \epsilon_{lg0}$  /2,  $\theta_{n+}$ ,  $\Delta \epsilon_{lg0}$ ,  $-\Delta \epsilon_{lg}$  ( $\theta_{0m}$ ) or the sum of 185 several singular values as observed in liquid elements and as expected from hidden 186 thresholds of configurons [78,79]. The crystallization enthalpy at  $T_{\times}$  of the liquid phase 187 coexisting with glassy Phase 3 is given by (18): 188

$$H_{cr} = H_m(-1 + \Delta \varepsilon), \tag{18}$$

The melting heat  $H_{3m}$  of each Phase 3 depends on its singular value and its contribution to  $\Delta \varepsilon$  at Tx. This melting, depending on the heating rate, occurs at various reduced 190 temperatures  $\theta_{n+}$  defined for each singular value of  $\Delta \varepsilon$  or is associated with other singular 191 values or leads to a unique melting temperature  $\theta_{n+} = \Delta \varepsilon$ : 192

$$H_{3m} = H_m \times \theta_{n+\prime} \tag{19}$$

The temperature  $T_x$  separates the two domains of glassy phases between  $T_g$  and  $T_{n+}$ . 193 Below  $T_g = T_x$ , the bulk glassy domain takes place after the fist-order transition at  $T_x$  while 194 the glassy fractions induced at  $T_x$  disappear at  $T_{n+}$  without attaining the virtual glass transition temperature  $T'_g$  equal to  $(2T_m - T_g)$ . The glass enthalpy disappears at  $T_{n+} < T'_g$  by heating from  $-\Delta \varepsilon H_m$  to 0 giving rise to homogeneous liquid. 197

# 4. 4- Gleaning information in published works to predict the crystallized fraction198from the knowledge of Tx or melting temperatures of various Phases 3 above Tm199

#### 4.1. Three melting temperatures of bismuth were observed above $T_m$ in two different experiments 200

DSC measurements of bismuth with a heating rate of 0.083 K/s showed two endothermic transitions at  $T_{1n+}=504.9$  °C (778 K) and  $T_{2n+}=511.5$  K (784.6 K) above the melting temperature  $T_m=544.5$  K as shown in Figure 1 [39]. A third transition were observed with the density at  $T_{3n+}=1013$  K in another experiment in the absence of transformations at  $T_{1n+}=204$ and  $T_{2n+}$  [40].



Figure 1. Experimental results for DSC of bismuth. Reproduced with permission from [ (39)] Figure2072a. Copyright 2004 Elsevier.208

With the model already developed for other liquid elements [79], these temperatures 209 are used to calculate a Bi Lindemann coefficient equal to 0.09119 in good agreement with 210 the value 0.095 recently found [92]. The glass transition temperature is predicted at  $T_g$ = 211 203.5 K and the singular enthalpy coefficients  $\Delta \varepsilon$  are  $\Delta \varepsilon_{ig0} = 0.1907$ ,  $-\Delta \varepsilon_{ig}(\theta_g) = 0.094065$ , -212  $\Delta \epsilon_{lg} (\theta_{0m} = -2/3) = 0.10594$  and  $-\Delta \epsilon_{lg} (\theta = -1) = 0.238375$ . The experimental coefficients  $\Delta \epsilon$  giving 213 rise to  $\theta_{1n+}$ = 778/544.5 -1= 0.429 and  $\theta_{2n+}$ = 784.6/544.5 -1= 0.44096 are equal to the theoretical 214 ones 0.1907+0.238375 = 0.429075 and 0.094065+0.10594+0.238375= 0.43838 respectively. The 215 total glassy fraction melted at the two temperatures Tn+ represent 86.7% while the crystal-216 lized fraction melted at  $T_m$  would be 13.3%. The transition at  $T_{3n+}$  is expected at  $\theta_{3n+} = 0.8675$ 217  $(T_{3n+}=1.8675T_m)$  corresponding to 1016 K in the absence of transitions at  $T_{1n+}$  and  $T_{2n+}$  in 218 agreement with the second experiment. The formation of distinct glassy phases with sin-219 gular enthalpies at Tx depends on the heating rate. 220

## 4.2. Crystallization enthalpy reduction of $Pd_{40}Ni_{40}P_{20}$ at the temperature $T_x$ after quenching and 221 various annealing of the same duration at lower temperatures 222

The bulk melting temperature is  $T_m = 870$  K; the glass transition temperature of ribbons is  $T_g = 575$  K ( $\theta_g = -0.33909$ ) and the virtual glass transition temperature  $T'_g = 2T_m - T_g =$ 1165 K ( $\theta_{n+} = 0.33909$ ). The first-order transition at  $T_x$  is unique and shown in Figure 2 [93]. 225 An endothermic transition was observed at  $T_{1n+} = 984$  K above  $T_m$  [94]. The enthalpy coefficients are calculated using (9,10,12,13),  $\theta_g = -0.33908$  and a = 1. Liquids 1, 2, and 3 obey (20,21,22) respectively: 228

$$\varepsilon_{\rm ls} = 1.66092(1 - \theta^2/0.250305),$$
 (20)

$$\varepsilon_{\rm gs} = 1.49138(1 - \theta^2/0.33713),$$
 (21)

$$\Delta \varepsilon_{\rm lg}(\theta) = \left[\varepsilon_{\rm ls} - \varepsilon_{\rm gs}\right] = \left[0.16954 - \Delta \varepsilon - 2.2118 \times \theta^2\right]. \tag{22}$$



Figure 2. The DSC traces of the as-prepared Pd40Ni40P20 ribbon glass reproduced with permission230from [93]. Samples annealed at different temperatures in the supercooled liquid region for 30231minutes and heated from 300 K at a heating rate of 20 K/min under a flow of purified argon. Copy-232right 2002 AIP Publishing.233

The first-order transition at  $T_x$ = 639 K, driven by the entropy of Phase 3, counted from its 234 formation temperature at 529.36 K, being equal to  $(\Delta \epsilon_{lg}-0.21614) \times H_m/T_x$ , leads to a singular 235 enthalpy of Phase 3 equal to -0.21614×Hm [64,65]. The singular enthalpy coefficients,  $\Delta \epsilon$ = 236  $\theta_{n+}$  are: 0,  $\Delta \epsilon_{lg0}/2 = 0.08477$ , 0.13197,  $\Delta \epsilon_{lg0} = 0.16984$ ,  $-\Delta \epsilon_{lg}$  ( $\theta_{0m}$ ) = 0.38409 and the sums 237 0.13137+0.08477= 0.21614 and 0.38409 + 0.16954 + 0.13197 + 0.08477= 0.76977. The crystalli-238 zation enthalpies roughly correspond to these singular values of  $\theta_{n+}$  as shown in Figure 3 239 with (18) respected. Additional melting temperatures are also predicted above Tm. The 240 transition at T<sub>x</sub> is sharp in Figure 2 up to T<sub>a</sub>= 618 K ( $\Delta \epsilon = \theta_{n+} = 0.16954$ ) and more broaden 241 above. The transition at  $\theta_{n+}$  above T<sub>m</sub> is expected to be observable up to  $\theta'_g = 0.33909 = 2T_m$ -242 T<sub>g</sub>. Too-high Higher values of  $\Delta \varepsilon$  above  $\theta'_{g}$  led to higher fractions of crystalline phase. 243

The first-order transition at  $T_x$  is expected to induce a glassy fraction of 33.909 % 244 which melts at  $T_{n+}= 0.33909$ . The crystallization enthalpy, after various annealing, is 245 strongly reduced because it roughly cumulates several singular values of  $\Delta \epsilon$  below  $\theta_{n+}=1$  246 when the annealing temperature  $T_a$  passes 623 K. 247

#### Crystallization enthalpy in J/g of Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> ribbon



248

Figure 3. Crystallization enthalpies  $H_{cr}$  in J/g, measured in Pd40Ni40P20 ribbon by [93] versus the249glassy Phase 3 melting at  $\theta_{n+}$  and calculated with (18). The singular enthalpy coefficients are deduced250from (27-29). The experimental uncertainty on  $H_{cr}$  is ±5 J/g. Crystallizations for  $\Delta \epsilon$ = 0.76977 and2510.38409 occurring at Tx. Values of  $H_{cr}$  taken from [93] Figure 3.252

#### 4.3. Melting temperatures of Co<sub>76</sub>Sn<sub>24</sub> above T<sub>m</sub>= 1392 K

The melting temperature of Co<sub>76</sub>Sn<sub>24</sub> is  $T_m = 1382$  K. The first temperature  $T_{1n+}$  of this 254 alloy is observed at 1583 ±10 K accompanied by an endothermic enthalpy [83,95]. Using 255 (23) [55], the glass transition temperature  $T_g$  is predicted as being equal to 866.9 K ( $\theta_g$ = - 256 0.37275) for  $T_{n+}$ = 1581.6 K ( $\theta_{n+}$ = 0.14441) while the virtual glass transition is (2T<sub>m</sub>-T<sub>g</sub>) = 257 1897.14 K: 258

$$\theta_{n+} = -0.38742 \times \theta_g. \tag{23}$$

The enthalpy coefficients are calculated using (9,10,12,13) and a= 1. Liquids 1, 2, and 259 3 obey (24,25,26) respectively: 260

$$\varepsilon_{\rm ls} = 1.62725(1 - \theta^2 / 0.26958), \tag{24}$$

$$\varepsilon_{\rm gs} = 1.44088(1 - \theta^2 / 0.35806), \tag{25}$$

$$\Delta \varepsilon_{\rm lg}(\theta) = \left[\varepsilon_{\rm ls} - \varepsilon_{\rm gs}\right] = \left[0.18637 - 2.0121 \times \theta^2\right]. \tag{26}$$

The singular values of the enthalpy coefficient  $\Delta \varepsilon_{lg}$  ( $\theta$ ) are:  $\Delta \varepsilon_{lg}$  ( $\theta_g$ ) =  $-\Delta \varepsilon_{lg0}$  /2= - 261 0.18637/2 for a stable glass,  $\Delta \varepsilon_{lg}$  ( $\theta_{1n+}$ ) = -0.14441,  $\Delta \varepsilon_{lg0}$ = -0.18637 for an ultra-stable glass, 262  $\Delta \varepsilon_{lg}$  ( $\theta_{0m}$ ) = -0.35605. Two first-order transition temperatures were observed at T<sub>n</sub>= 1129 K 263 and 1263 K by supercooling [83,95]. They are predicted using (14) with the singular values 264 of  $\Delta \varepsilon = \theta_{n+} = 0.14441$  and 0.33078= 0.14441+0.18637. The transition for  $\Delta \varepsilon_{lg} = -0.35605$  does not 265 exist because it would lead to a second melting temperature higher than the glass transition T'<sub>g</sub>= 1897.14 K. 267

The equations (27,28,29) used to predict Phase 3 enthalpy decreasing with temperature are determined with  $\theta_g$ = 0.37275 (T<sub>g</sub>= 1897.14 K) and (9,10,12,13). 269

$$\varepsilon_{\rm ls} = 2.37275(1 + \theta^2 / 0.34266), \tag{27}$$

$$\varepsilon_{\rm gs} = 2.49617(1 - \theta^2/0.55046),$$
 (28)

$$\Delta \varepsilon_{\rm lg}(\theta) = \left[\varepsilon_{\rm ls} - \varepsilon_{\rm gs}\right] = \left[-0.18637 + 2.0121 \times \theta^2\right]. \tag{29}$$

Lines 1 and 2 determined by (26) and (29) in Figure 5 are obtained by heating from 270 various glassy states depending on thermal history and heating rate and leading to exo-271 thermic or endothermic transitions at  $T_{1n+}$ = 1581.6 K. An endothermic transition was observed at  $T_{1n+}$ [95]. 273

The transformation at Tx of Phase 3 by heating from the glassy state is predicted using 274 (14) with  $\Delta \epsilon = 0.33078 = 0.14441 + 0.1837$ ,  $\epsilon_{1s0} = 1.44088$ , and  $\theta_{0g}^2 = 0.35806$  and leads to a negative enthalpy coefficient equal to -0.33078 as shown in Figure 4. The enthalpy of Phase 3, 276  $0.33078 \times H_m$ , would be recovered at the second melting temperatures  $T_{n+} = 1581.6 \text{ K}$  ( $\theta_{n+} = 0.18637$ ). The melting enthalpy of the crystallized part would be (1-0.33078) Hm = 0.66933 \times Hm while the crystallization enthalpy would be  $-0.66933 \times H_m$ . 279

The temperatures  $T_x$  would separate two domains of glassy states. The melt would 280 be fully glassy below  $T_x$  after transition at  $T_x$  and partially glassy from  $T_x$  to  $T_{n+}$ . The glassy 281 fractions of the melt would be 33.078% from  $T_x$  to 1581.6 K and 18.637% from 1581.6 to 282 1639.6 K. 283

253



Figure 4. Phase 3 enthalpy coefficients above the temperatures T<sub>1x</sub> and T<sub>2x</sub>. T<sub>1x</sub>= 1263 K, T<sub>2x</sub>= 1382 K, 285  $T_{1n+}=$  1581.6 and  $T_{2n+}=$  1639.6 K. Lines 1 and 2 calculated with equations (26,29) in the absence of 286 transition at Tx. Glassy state of 33.078% of the melt up to 1581.6 K and 18.637% from 1581.6 to 1639.6 287 K. Lines 1 and 2 without transition at Tx corresponding to 14.441% of glassy Phase 3. 288

#### 4.4. Melting temperatures of $Bi_2Te_3$ and its alloys above $T_m = 864 \text{ K}$

Liquid-liquid structure transitions in metallic melts have an impact on solidification 290 [96] and play an important role in the final microstructure and the properties of the solid 291 alloys. We note that the compound Bi<sub>2</sub>Te<sub>3</sub> is used for the most of Peltier cooling devices 292 and thermoelectric generators. In alloys based on this compound, during the first heating 293 process, a temperature-induced liquid-liquid structural transition existed at a tempera-294 ture that we call T<sub>1n+</sub> which disappeared in the resistivity measurements by cooling from 295 higher temperatures than T<sub>n+</sub> [44,45]. Solidifying at various cooling rates in these condi-296 tions, the microstructures were refined, and the hardness increased with cooling rate. The 297 glass transition temperature of Bi2Te3 and its alloys were unknown. Applying (23) to this 298 compound with  $T_m$ = 864 K and  $T_{1n+}$ = 967.8 K [97], the two glass transition temperatures 299 are predicted at  $\theta_g$ = -0.29576 (T<sub>g</sub>= 586 K) and  $\theta'_g$ = 0.29576 (T'<sub>g</sub>= 1132 K). The presence of 300 nucleation and recalescence temperatures and a temperature of recalescence below T<sub>m</sub> 301 upon cooling was dependent on cooling rate. The exothermic transition at Tn+ was also 302 observed by DSC during cooling at 135 K/min.

The equations (30,31,32) used to predict Phase 3 enthalpy increasing with temperature are determined with  $\theta_g$ = -0.29576 (T<sub>g</sub>= 586 K) and (9,10,12,13):

> $\varepsilon_{ls} = 1.68981(1 - \theta^2/0.23296),$ (30)

$$\varepsilon_{\rm gs} = 1.53472(1 - \theta^2/0.31736),$$
 (31)

$$\Delta \varepsilon_{\rm lg}(\theta) = \left[\varepsilon_{\rm ls} - \varepsilon_{\rm gs}\right] = \left[0.15509 - 2.4179 \times \theta^2\right]. \tag{32}$$

The singular values of the enthalpy coefficient  $\Delta \varepsilon_{lg}$  ( $\theta$ ) are:  $\Delta \varepsilon_{lg}$  ( $\theta_g$ ) =  $-\Delta \varepsilon_{lg0}$  /2= 306 -0.15509/2,  $-\Delta \epsilon_{lg} (\theta_{n+}) = -0.12017$ ,  $-\Delta \epsilon_{lg0} = -0.15509$ ,  $\Delta \epsilon_{lg} (\theta_{0m}) = -0.40818$ . The first-order transi-307 tion for  $\Delta \varepsilon = 0.40818$  does not exist because it would lead to a second melting temperature higher the second glass transition T'g at 1897.1 K. It is replaced by a first-order transition 309 with  $\Delta \varepsilon = 0.12017 + 0.15509 = 0.27527$ . Two first-order transition temperatures are expected 310 for  $\theta_{n+} = \Delta \varepsilon = 0.12017$ ) and  $\theta_{n+} = \Delta \varepsilon = 0.27527$ . 311

The equations (33,34,35) used to predict Phase 3 enthalpy decreasing with tempera-312 ture are determined with  $\theta_g$ = 0.29576 (T<sub>g</sub> = 1132 K) and (9,10,12,13). 313

$$\varepsilon_{\rm ls} = 2.31019(1 + \theta^2/0.31848) \tag{33}$$

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$$\varepsilon_{\rm gs} = 2.46528(1 - \theta^2/0.5098),$$
 (34)

$$\Delta \varepsilon_{\rm lg}(\theta) = \left[\varepsilon_{\rm ls} - \varepsilon_{\rm gs}\right] = \left[-0.15509 + 2.4179 \times \theta^2\right]. \tag{35}$$

Lines 1 and 2 determined by (32) and (35) in Figure 5 obtained by heating from the 314 glassy state, depend on thermal history and heating rate and lead to exothermic and endothermic transitions at  $T_{1n+}$ = 967.8 K. 316

The crystallization of Phase 3 by heating from the glassy state is predicted at Tx= 802 317 K using (14) with  $\Delta \epsilon$ = 0.12017+0.15509= 0.27527,  $\epsilon_{1s0}$ = 1.53472, and  $\theta_{0g}$ <sup>2</sup>= 0.31736 and lead to 318 the negative enthalpy coefficient, -0.27527, as shown in Figure 5. This transition at 802 K 319 was observed by supercooling at 135 K/min [ (97)] and was viewed as the nucleation tem-320 perature of nanocrystals. The glassy enthalpy -0.27527×Hm would be recovered at the sec-321 ond melting temperatures  $T_{n+}$  = 967.9 K ( $\theta_{n+}$  = 0.12017) and 998 K ( $\theta_{n+}$  = 0.15509). The melting 322 enthalpy of the crystallized part would be (1-0.27527) H<sub>m</sub> = 0.72473×H<sub>m</sub> while the crystal-323 lization enthalpy would be -0.72473×Hm. 324



Figure 5. Phase 3 enthalpy coefficients above the temperature  $T_x$ .  $T_x$ = 802 K,  $T_m$  = 864 K,  $T_{AB}$  = 874.4326K,  $T_{n+}$  = 967.9 and 998 K. Lines 1 and 2 in the absence of transition at  $T_x$ . Glassy state of 27.527% of327the melt up to 967.9 K and 15.509% from 967.9 to 998 K. Lines 1 and 2 without transition at  $T_x$  corresponding to 12.017% of glassy Phase 3.328

#### 4.5. The six melting temperatures of Zr<sub>46</sub>Cu<sub>46</sub>Al<sub>8</sub> above 1200 K

The glass transition temperature of  $Zr_{46}Cu_{46}Al_8$  is  $T_g$ = 715 K. There are three melting 331 temperatures 962 K, 1034 K and 1125 K as shown in Figure 6 inducing three unknown 332 Phases 3 observed with heating rates between 0.1666 and 2 K/s in this non-congruent alloy 333 and three theoretical virtual glass transition temperatures equal to 1209 K, 1353 K, and 334 1535 K respectively [98]. Consequently, there are different coefficients  $\varepsilon_{1s0}$ ,  $\varepsilon_{gs0}$ ,  $\theta_{0g^2}$ ,  $\theta_{0m^2}$ , 335  $\Delta \varepsilon_{lg}$  ( $\theta_{0m}$ ),  $\Delta \varepsilon = \theta_{n+}$  for every one of them given in Table 1 and calculated with (9, 10, 12, 13, 336 15), a= 1 and  $\theta_g$ = -0.25676 for T<sub>m</sub> =962 K, -0.30851 for T<sub>m</sub> = 1034 K and -0.36444 for T<sub>m</sub> = 1125 337 K. The main phase having the highest melting enthalpy corresponds to  $T_m$  =1125 K. 338



Figure 6. DSC of Zr46Cu46Als in green around the melting temperatures using heating rates between3400.166 and 2 K/s. Reproduced with permission from [98] "XRD patterns and DSC curves of the arc-341melted Zr46(Cu4.5/5.5 Ag1/5.5)46Als ingot and as-cast Zr46(Cu4.5/5.5 Ag1/5.5)46Als BMG sample, together with342DSC curve of as-cast Zr46Cu46Als BMG alloy". Melting temperatures of 3 phases in Zr46Cu46Als: 962343K, 1034 K and 1125 K. Copyright 2008 Elsevier.344

Table 1. Multiple melting temperatures Tm and Tn+ of Cu46Zr46Als. Tg = 715 K; Tm, the first melting345temperature;  $\theta_g$ , the reduced glass transition temperature;  $\mathcal{E}_{Is0}$ ,  $\theta_{0m}^2$ ,  $\mathcal{E}_{gs0}$ ,  $\theta_{0g}^2$  calculated with346(9,10,12,13);  $\Delta \mathcal{E}_{Ig}$  ( $\theta_{0m}$ ) with (15), the enthalpy coefficient of Phase 3 at  $\theta = \theta_{0m}$ ;  $\Delta \mathcal{E} = \theta_{n+}$  the enthalpy347coefficient singular values of glassy Phase 3 above  $T_x = 763$  K;  $T_{n+}$  (K), the theoretical second melting348temperatures; Obs., with yes when  $T_{n+}$  has been observed in Figure 7; T'g, the virtual glass transition349temperature above  $T_{n+}$ .

Tg	Tm	$\theta_{\mathrm{g}}$	Els0	$\theta_{om}^2$	Egs0	$\theta_{og}{}^2$	$\Delta \epsilon_{lg} \left( \theta_{0m} \right)$	$\Delta \epsilon {=}  \theta_{n{\scriptscriptstyle +}}$	$T_{n^+}$	Obs.	T'g
715	962	-025676	1.74324	0.19893	1.61486	0.27642	-0.4527	0.06419			1209
715	962	-0.25676	1.74324	0.19893	1.61486	0.27642	-0.4527	0.09947	1057		1209
715	962	-0.25676	1.74324	0.19893	1.61486	0.27642	-0.4527	0.12838	1086		1209
715	962	-0.25676	1.74324	0.19893	1.61486	0.27642	-0.4527	0.22785	1181		1209
715	1034	-0.30851	1.69149	0.23193	1.53723	0.31617	-0.40957	0.07713			1353
715	1034	-0.30851	1.69149	0.23193	1.53723	0.31617	-0.40957	0.11953	1158		1353
715	1034	-0.30851	1.69149	0.23193	1.53723	0.31617	-0.40957	0.15426	1194		1353
715	1034	-0.30851	1.69149	0.23193	1.53723	0.31617	-0.40957	0.19665	1237	Yes	1353
715	1034	-0.30851	1.69149	0.23193	1.53723	0.31617	-0.40957	0.27378	1317	Yes	1353
715	1125	-0.36444	1.63556	0.26492	1.45333	0.35311	-0.36296	0.09111			1535
715	1125	-0.36444	1.63556	0.26492	1.45333	0.35311	-0.36296	0.1412	1284	Yes	1535
715	1125	-0.36444	1.63556	0.26492	1.45333	0.35311	-0.36296	0.18222	1330	Yes	1535
715	1125	-0.36444	1.63556	0.26492	1.45333	0.35311	-0.36296	0.32342	1489	Yes	1535
715	1125	-0.36444	1.63556	0.26492	1.45333	0.35311	-0.36296	0.36296	1533	Yes	1535





Figure 7. Melt phase transitions in  $Cu_{46}Zr_{46}Al_8$  above 1200 K. Reproduced with permission from353[41]. "Melt phase transitions in  $Cu_{46}Zr_{48}Al_4$  and  $Cu_{46}Zr_{46}Al_8$ . The DSC upon cooling for  $Cu_{48}Zr_{48}Al_4$ 354(red one) and  $Cu_{46}Zr_{46}Al_8$  (black one) melts in arbitrary unit (AU) upon cooling from 1623 K with a3550.167 K/s rate". Copyright 2014 American Physical Society. Peaks numbered 1 to 6 for  $Cu_{46}Zr_{46}Al_8$ 356with predicted temperatures  $T_{n+}$ : for  $T_m$ = 1125 K (N°2-1284K, N°4-1330 K, N°5-1489 K, N°6-1533 K);357for  $T_m$ = 1034 K (N°1- 1237 K, N°3- 1317 K) and for  $T_m$ = 962 K, no temperature  $T_{n+}$  above 1200 K.358Copyright 2013 AIP Publishing.359

Six first-order transition temperatures accompanied by exothermic latent heats were 360 observed above 1200 K by cooling the melt from 1650 K as shown in Figure 7 [41]. These 361 temperatures predicted in Table 1 are melting temperatures upon heating. Peaks num-362 bered 1 to 6 correspond to predicted temperatures  $T_{n+}$ : for  $T_m$ = 1125 K (N°2-1284K, N°4-363 1330 K, N°5- 1489 K, N°6- 1533 K); for T<sub>m</sub>= 1034 K (N°1- 1237 K, N°3- 1317 K) and for T<sub>m</sub>= 364 962 K, no  $T_{n+}$  above 1200 K. Peaks N°s1 and 3 are weak compared to N°s2, 4, 5 and 6. The 365 sum of predicted enthalpy coefficients of peaks N°s2, 4, 5 and 6 is equal to -0.1412-0.18222-366 0.32342-0.36293= -1.0098≅ -1 below T<sub>1n+</sub>= 1284 K instead of T<sub>m</sub> = 1125 K in good agreement 367 with the melting of a glass having an enthalpy coefficient equal to -1, the enthalpy coeffi-368 cient of full crystallization. A full glassy state exists below T<sub>1n+</sub> = 1284 K and then, the glassy 369 state fraction declines with three increases of  $T_{n+}$  from  $T_{1n+}$  to  $T_{4n+}$  = 1533 K. 370

All transitions of Phases 3 with Tm= 1125 K are represented in Figure 8. Lines 1 and 2 371 represent Eqs. (15,16). The transition at  $T_x = 760.3$  K occurs when  $\Delta \varepsilon_{lg} = 0$  for the phase 3 372 enthalpy coefficient corresponding to the lowest melting temperature T<sub>m</sub>= 962 K. The for-373 mation, by heating, of a glass phase having an enthalpy equal to that of crystals, occurs 374 using heating rates inducing a first-order transition at Tx without crystallized fraction-375 The observation of glass fractions melting above T<sub>m</sub> could be obtained by heating because 376 all first-order transitions at Tn+ were reversible and corresponded to singular enthalpies of 377 the glassy phase and probably various percolation thresholds [41]. The first-order transi-378 tion at T<sub>x</sub>= 760.3 K leading to a glassy fraction equal to 100 % corresponds to  $\Delta \varepsilon$ = -1 at a 379 temperature far below  $T_m$  = 1125 K using a low heating rate. Nevertheless, a crystallization 380 enthalpy occurs at T<sub>m</sub> = 1125 K as shown in Figure 6 because the melt, in this case, has not 381 been overheated above  $T_{4n+}$ = 1533 K before cooling [98]. The glassy state obtained at  $T_x$ = 382 760.3 K could totally escape crystallization following the red broken line N°3 using low 383 heating rates such as 0.333 K/s if the melt is previously overheated above T'  $_g$ = 1535 K be-384 fore cooling as shown in Figure 7. 385



Figure 8. Multiple transitions and glassy states expected in the melt fraction with  $T_m$ = 1125 K of387Cu<sub>46</sub>Zr<sub>46</sub>Al<sub>8</sub>. Eq. (15,16) represented by Lines 1 and 2 using enthalpy coefficients given in Table 1 for388T<sub>m</sub>= 1125 K. Glass states of Phases 3 noted 3, 4, 5, and 6. T<sub>0m</sub>= 545.9; T<sub>3</sub>= 651.6 K; T<sub>g</sub>= 715 K; T<sub>x</sub>= 760.3389K; T<sub>m</sub>= 1125 K; T<sub>1n+</sub> = 1283.9; T<sub>2n+</sub>= 1330 K; T<sub>3n+</sub>= 1488.8 K; T<sub>4n+</sub>= 1533.3 K. The reversible red broken390Line N°3 observed above 1200 K with cooling and heating rates of 0.333 K/s in Figure 7.391

The first order transitions are due to liquid super atom formation at  $T_{n+}$ . Observations of 392 multiple temperatures  $T_{n+}$  are facilitated in this alloy because they have a first-order character much stronger than those observed in La<sub>50</sub>Al<sub>35</sub>Ni<sub>15</sub> and Pd<sub>42.5</sub>Ni<sub>42.5</sub> P<sub>15</sub> studied by 394 [37,38] due, here, to the spontaneous formation and percolation of solid super atoms instead of having bonds progressively built-in liquid super atoms (clusters-bound colloids) 396 during slow cooling [77]. 397

#### 5. Conclusions

This paper is devoted to liquid-liquid transitions in glass-forming melts. A first liquid-liquid transition was often observed at a temperature  $T_{In+}$  above the equilibrium thermodynamic transition  $T_m$  after heating from the glassy state without previous first-order transition at a temperature  $T_x$  weaker than  $T_m$ . This transition at  $T_{n+}$  was exothermic or endothermic and associated with antibonds or bonds breaking predicted by the non-classical nucleation model and in agreement with the configuron percolation model as already shown in previous publications.

Separation phenomena were observed by molecular dynamics simulations of mono-406 atomic liquid elements at very high heating rates and still predicted. Full melting of Ag, 407 Cu, Zr and Fe were obtained at temperatures much higher than Tm showing that the crys-408 tal fraction can fully profit from the disappearance of any glass phase above T<sub>m</sub>. An in-409 crease in the melting temperature of glassy phases at high heating rate is due to finite mo-410bility of configurons - broken chemical bonds, which at relatively low heating rates 411 quickly condense causing the typical first-order phase transformation arrest at the tem-412 perature  $T_x$ . At higher heating rates however, there is not enough time for condensation 413 to occur and thus the melting occurs at a much higher temperature when the percolation 414 via configurons occurs. 415

In this paper, some mysterious aspects of the first-order transition occurring at  $T_x$  and 416 leading to crystallization were enlightened, considering phase separation between a 417 glassy fraction having a glass transition temperature higher than  $T_m$  and a second fraction, 418 crystallizing at  $T_x$ , and melting at  $T_m$ . The non-classical nucleation model predicts the existence of two glassy phases at  $T_g$  and  $T'_g$  in two different temperature domains separated 420 by the temperature  $T_x$ . The transition at  $T_x$  increases  $T_g$  up to  $T_x$  and induces a new glassy 421

phase above  $T_x$ . The temperature  $T'_g$  is virtual because the glass phase has a melting temperature higher than  $T_m$  and lower than  $T'_g$ . 423

These new melting temperatures are observable at Tn+ at low heating rates as already 424 anticipated by the reduction of the crystallization enthalpy of some monoatomic elements 425 after supercooling and recalescence. Several new examples were found in publications. 426 Three liquid-liquid transitions in bismuth observed in two different experiments lead to 427 a total glassy fraction of 86.7% and a melting temperature equal to  $1.867T_{\rm m}$  in one of the 428 two experiments and to 1.438Tm in the other. Four reversible first-order liquid-liquid tran-429 sitions in Cu<sub>46</sub>Zr<sub>46</sub>Al<sub>8</sub> lead to a glassy fraction of 100 %, for the phase with T<sub>m</sub>= 1125 K and 430 a melting temperature of 1.36Tm. Predictions of complementary liquid-liquid transitions 431 were made for Co76Sn24, Pd40Ni40P20, and Bi2Te3 beyond the first liquid-liquid transitions 432 already observed. 433

The first-order transitions at Tx observed by heating were accompanied by latent 434 heats composed of singular values of the glass enthalpy or of their sum as already shown 435 for monoatomic elements. They determined the first-order liquid-liquid transitions at Tn+ 436 above  $T_m$  which were reversible in  $Cu_{46}Zr_{46}Al_8$  and observed with the same latent heats by 437 cooling from homogeneous liquid state and heating due the melting and formation of 438 percolating solid superclusters (superatoms)respectively. The same transitions at  $T_{n+}$  ob-439 served in La50Al35Ni15 and Pd42.5Ni42.5 P15 involve much weaker latent heats by cooling be-440cause percolating liquid superclusters (superatoms) formed at Tn+ from homogeneous liq-441 uid are progressively solidified by cooling from Tn+ instead of being fully solidified at Tn+. 442

The melts are rejuvenated above  $T'_g = 2T_m - T_g$  because all growth nuclei of crystals are eliminated by superheating above  $T'_g$ . Many techniques of quenching, used up to now, to escape crystallization, do not overheat melts far above  $T_m$  before quenching and are not able to reveal the various glassy states above  $T_x$ . 443

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