Building and Breaking Bonds by Homogenous Nucleation in Glass-Forming Melts Leading to Transitions in Three Liquid States

Robert F. Tournier 1,*, and Michael I. Ojovan 2,3 *

1 LNFC-EMFL, CNRS, Université Grenoble Alpes, INSA-T, UPS, 38042 Grenoble, France
2 Department of Materials, Imperial College London, London SW7 2AZ, UK; m.ojovan@imperial.ac.uk
3 Department of Radiochemistry, Lomonosov Moscow State University, 119991 Moscow, Russia
* Correspondence: robert.tournier@lnfc.cnrs.fr

Abstract: The thermal history of melts leads to three liquid states above the melting temperatures $T_m$ containing clusters—bound colloids with two opposite values of enthalpy $+\Delta \varepsilon_{lg} \times \Delta H_m$ and $-\Delta \varepsilon_{lg} \times \Delta H_m$ and zero. All colloid bonds disconnect at $T_n+ > T_m$ and give rise in congruent materials, through a first-order transition at $T_{LL} = T_{n+}$, forming a homogeneous liquid, containing tiny superatoms, built by short-range order. In non-congruent materials, $(T_n+)$ and $(T_{LL})$ are separated, $T_n+$ being the temperature of a second order and $T_{LL}$ the temperature of a first-order phase transition. $(T_n+)$ and $(T_{LL})$ are predicted from the knowledge of solidus and liquidus temperatures using non-classical homogenous nucleation. The first-order transition at $T_{LL}$ gives rise by cooling to a new liquid state containing colloids. Each colloid is a superatom, melted by homogeneous disintegration of nuclei instead of surface melting, and with a Gibbs free energy equal to that of a liquid droplet containing the same magic atom number. Internal and external bond number of colloids increases at $T_n+$ or from $T_n+$ to $T_g$. These liquid enthalpies reveal the natural presence of colloid–colloid bonding and antibonding in glass-forming melts. The Mpemba effect and its inverse exist in all melts and is due to the presence of these three liquid states.

Keywords: liquid–liquid transitions; glass phase; amorphous; undercooling; superheating; percolation threshold; microheterogeneity

1. Introduction

Glass-forming melt transformations have been mainly studied, for many years, around the glass transition temperature $T_g$ and sometimes up to the liquidus temperature $T_{liq}$. The liquid properties are often neglected because the classical nucleation equation predicts the absence of growth nuclei and nucleation phenomenon above the melting temperature. The presence of growth nuclei above $T_m$ being known [1–3], an additional enthalpy is added to this equation to explain these observations. A new model of nucleation is built from the works of Turnbull’s [4] characterized by two types of homogeneous nucleation temperatures below and above $T_m$. The new additional enthalpy is a quadratic function of the reduced temperature $\theta = (T - T_m)/T_m$ as shown by a revised study of the maximum undercooling rate of 38 liquid elements using Vinet’s works [5,6]. A concept of two liquids is later introduced to explain the glass phase formation at $T_g$ by an enthalpy decrease from liquid 1 to liquid 2 at this temperature. New laws minimizing the numerical coefficients of each quadratic equation are established determining the enthalpies $\varepsilon_{lg}(0) \times \Delta H_m$ of liquid 1 and $\varepsilon_{lg}(0) \times \Delta H_m$ of liquid 2 for each $\theta$ value, with $\Delta H_m$ being the melting enthalpy [7,8]. The thermodynamic transition at $T_g$ is characterized by a second-order phase transition and a heat capacity jump defined by the derivative of the difference $(\varepsilon_{lg}(\theta) - \varepsilon_{lg}(\theta))\Delta H_m$, which is equal to 1.5 $\Delta S_m$ for many glass transitions with $\Delta S_m$ being the melting entropy [9].

The glass transition results from the percolation of superclusters formed during cooling below $T_m$ [10–12]. A thermodynamic transition characterized by critical parameters occurs by breaking bonds (configurons) and when the percolation threshold of configurons
is attained [13–17]. Building bonds by enthalpy relaxation below $T_g$ has for consequence the formation of a hidden undercooled phase called phase 3 with an enthalpy $(\varepsilon_{ls}(\theta) - \varepsilon_{gs}(\theta)) \Delta H_m$ equal to that of configurons with a residual bond fraction which can be overheated up to $T_{n^+} > T_m$ before being melted [18]. The homogeneous nucleation temperature at $T_{n^+}$ occurs in overheated liquids and is predicted for many molecular and metallic glass-forming melts.

This paper is devoted to phase transitions above $T_m$, completing our recent work, showing that the dewetting temperatures of pre-frozen and grafted layers in ultrathin films are equal to $T_{n^+}$ [19]. The latent heats are exothermic or endothermic without knowing the explanation. The existence of a first-order transition is claimed for Pd$_{42.5}$Ni$_{42.5}$P$_{15}$ and La$_{50}$Al$_{35}$Ni$_{15}$ liquid alloys [20,21]. Our nucleation model of melting the liquid mean-range order by breaking residual bonds predicted all values of $T_{n^+}$ and exothermic enthalpies at this temperature. The observation of endothermic latent heats showed the existence of three liquid states at $T_m$, the first one with a positive enthalpy $\varepsilon_{gs}(0) \times \Delta H_m$, the second one zero, and the third one $-\varepsilon_{gs}(0) \times \Delta H_m$, which is negative. The liquid is homogeneous above $T_{n^+}$ when its enthalpy is equal to zero. The existence of various liquid states was also predicted without using a non-classical nucleation equation [22]. The formation temperature of a homogeneous liquid state was observed by measuring the density or the viscosity during heating and cooling, determining the point where the branching of these quantities disappears. Colloidal states were observed below this homogenization temperature and composed of thousands of atoms defining liquid heterogeneities [23–27]. Our objectives were to predict all these phase transitions.

2. The Homogeneous Nucleation

The Gibbs free energy change for a nucleus formation in a melt was given by Equation (1) [6,9]:

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

(1)

where $R$ is the nucleus radius and following Turnbull [4], $\sigma_{ls}$ its surface energy, given by Equation (2), $\theta$ the reduced temperature $(T - T_m) / T_m$, $\Delta H_m$ the melting enthalpy at $T_m$, and $V_m$ the molar volume:

$$\sigma_{ls}(V_m / N_A)^{-1/3} = \alpha_{ls} \Delta H_m / V_m$$

(2)

A complementary enthalpy $-\varepsilon_{ls} \times \Delta H_m / V_m$ was introduced, authorizing the presence of growth nuclei above $T_m$. The classical nucleation equation was obtained for $\varepsilon_{ls} = 0$.

The critical radius $R_{ls}^*$ in Equation (3) and the critical thermally activated energy barrier $\frac{\Delta G_{ls}^*}{k_B T}$ in Equation (4) are calculated assuming $d\varepsilon_{ls} / dR = 0$:

$$R_{ls}^* = \frac{-2\alpha_{ls}}{(\theta - \varepsilon_{ls}) (V_m / N_A)^{-1/3}}$$

(3)

$$\frac{\Delta G_{ls}^*}{k_B T} = \frac{16\pi \Delta S_m \alpha_{ls}^3}{3N_A k_B (1 + \theta) (\theta - \varepsilon_{ls})^2}$$

(4)

These critical parameters are not infinite at the melting temperature $T_m$ because $\varepsilon_{ls}$ is not equal to zero. The nucleation rate $J = K_v \exp(-\frac{\Delta G_{ls}^*}{k_B T})$ is equal to 1 when Equation (5) is respected:

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

(5)

The surface energy coefficient $\alpha_{ls}$ in Equation (2) is determined from Equations (4) and (5) and given by Equation (6):

$$\alpha_{ls}^3 = \frac{3N_A k_B (1 + \theta) (\theta - \varepsilon_{ls})^2}{16\pi \Delta S_m} \ln(K_v)$$

(6)
The nucleation temperatures \( \theta_n \) obtained for \( d\alpha_3^3/d\theta = 0 \) obeys (7):

\[
d\alpha_3^3/d\theta \sim (\theta_n+ - \theta_\text{ls})(3\theta_n- + 2 - \theta_\text{ls}) = 0
\] (7)

In addition to the nucleation temperature \( T_n \) below \( T_m \), the existence of homogeneous nucleation up to \( T_n \) above \( T_m \) was confirmed by many experiments, observing the undercooling versus the overheating rates of liquid elements and CoB alloys [28,29]. This nucleation temperature could have, for consequence, the possible existence of a second melting temperature of growth nuclei above \( T_m \) and of their homogeneous nucleation at temperatures weaker than \( \theta_{n+} \).

The coefficient \( \epsilon_\text{ls} \) of the initial liquid called liquid 1 is a quadratic function of \( \theta \) in Equation (8) [6]:

\[
\epsilon_\text{ls} = \epsilon_{ls0}(1 - \theta^2/\theta_{0m}^2)
\] (8)

where \( \theta_{0m} \) is the Vogel–Fulcher–Tammann-reduced temperature leading to \( \epsilon_\text{ls} = 0 \) for \( \theta = \theta_{0m} \), the VFT temperature \( T_{0m} \) of many fragile liquids being equal to \( \pm 0.77 \ T_g \). This quasi-universal value is known for numerous liquids including atactic polymers [30,31].

New liquid states are obtained for \( \theta = \theta_{n+} = \epsilon_\text{ls} \) and \( \theta = \theta_{n-} = (\epsilon_\text{ls} - 2)/3 \) with Equation (7). The reduced nucleation temperatures \( \theta_{n-} \) are solutions of the quadratic Equation (9):

\[
\epsilon_\text{ls}\theta_{n-}^2/\theta_{0m}^2 + 3\theta_{n-} + 2 - \epsilon_{ls0} = 0
\] (9)

There is a minimum value of \( \epsilon_{ls0} \) plotted as function of \( \theta_{0m} \) using (8) and \( \theta_{n-} = (\epsilon_\text{ls} - 2)/3 \), determining the relation (10) between \( \theta_{0m} \) and \( \epsilon_{ls0} \) for which the two solutions of (9) are equal in the two fragile liquids [8,32]. These values defined the temperature where the surface energy was minimum and \( \theta_{20m} \) and \( \epsilon_{ls0} \) obeyed Equations (10) and (11):

\[
\theta_{0m}^2 = \frac{8}{9}\epsilon_{ls0} - \frac{4}{9}\epsilon_{ls0}^2,
\] (10)

\[
\epsilon_{ls}(\theta = 0) = \epsilon_{ls0} = 1.5\theta_{n-} + 2 = a\theta_g + 2
\] (11)

The value \( a = 1 \) in the Equation (10) leads to \( T_{0m} = 0.769 \times T_g \) in agreement with many experimental values [9].

All melts and even liquid elements underwent, in addition, a glass transition because another liquid 2 existed characterized by an enthalpy coefficient \( \epsilon_g \) given by Equation (12), inducing an enthalpy change from that of liquid 1 at the thermodynamic transition at \( T_g \) [7,9,32]:

\[
\epsilon_g = \epsilon_{g0}(1 - \theta^2/\theta_{0g}^2)
\] (12)

\[
\theta_{0g}^2 = \frac{8}{9}\epsilon_{g0} - \frac{4}{9}\epsilon_{g0}^2
\] (13)

\[
\epsilon_g(\theta = 0) = \epsilon_{g0} = 1.5\theta_{n-} + 2 = 1.5\theta_g + 2
\] (14)

The difference \( \Delta \epsilon_\text{lg} \) in the Equation (15) between the coefficients \( \epsilon_\text{ls} \) and \( \epsilon_g \) determines the phase 3 enthalpy when the quenched liquid escapes crystallization:

\[
\Delta \epsilon_\text{lg}(\theta) = \epsilon_\text{ls} - \epsilon_g = \epsilon_{ls0} - \epsilon_{g0} + \Delta \epsilon - \theta^2\left( \frac{\epsilon_{ls0}}{\theta_{0m}^2} - \frac{\epsilon_{g0}}{\theta_{0g}^2} \right)
\] (15)

The coefficient \( \Delta \epsilon_\text{lg}(\theta) \) defined a new liquid phase called phase 3 undergoing a hidden phase transition below \( T_g \) and a visible one at \( \theta_{n+} \), occurring for \( \Delta \epsilon_\text{lg}(\theta) = \theta_{n+} \), as shown by Equation (7). This transition was accompanied by an exothermic latent heat equal to \( \Delta \epsilon_\text{lg}(\theta) \times \Delta H_m \) corresponding to about 15% of the melting heat [18]. Phase 3 was detected for the first time in supercooled water and associated with glacial phase formation [33–35] and recently appears as being associated with configuron formation [13–18]. The concept of configurons was initially proposed for materials with covalent bonds which can be either
intact or broken [36]; then, it was extended to other systems including metallic systems based on ideas of Egami on bonds between nearest atoms in metals [16,37]. Thus, it is generically assumed that the set of bonds in condensed matter has two states; namely, the ground state corresponding to unbroken bonds and the excited state corresponding to broken bonds. The set of bonds in condensed matter is described in such a way by the statistics of a two-level system [38,39] which are separated by the energy interval $G_d$. The two approaches converge because the Gibbs free energy of phase 3 is equal to $G_d$. Phase 3 is assumed to be the configuron phase which is preserved above $T_{m+}$ in a liquid with medium-range order up to a temperature $T_{m+}$. Both transition temperatures $T_g$ and $T_{m+}$ are accompanied by enthalpy or entropy changes of phase 3 and are predicted in many cases: Annealing above and below $T_g$, vapor deposition, formation of glacial and quasi-crystalline phases in perfect agreement with experiments. Any transformation of phase 3 changes the initial liquid enthalpy and rejuvenation at $T_g < T < T_{m+}$ does not lead to the enthalpy of the initial liquid [18].

Our new publication here was devoted to the simplest case where ultrastable glass and glacial phase are not formed. The value of $\theta_{n+}$ was maximum in this case because all transformations below $T_g$ and $T_{m}$ modified the liquid state and decrease $\theta_{n+}$ [19].

The heat capacity jump at $T_g$ was equal to $1.5 \times \Delta H_m/T_m$ in polymers as shown in 1960 by Wunderlich [40] and confirmed for many molecular glasses [9] (where $\Delta H_m/T_m = \Delta S_m$ is the crystal melting entropy). The contribution of the undercooled liquid to the total heat capacity per mole is given by (16) using $d\Delta e_{lg} (\theta)/dT$:

$$\Delta C_p(T) = C_p(liq) - C_p(cryst) = 2\left(\frac{T - T_m}{T_m^2}\right)(\Delta H_m)\left(\frac{\xi_{lg}}{\theta_{0m}^2} - \frac{\xi_{lg}}{\theta_{0g}^2}\right)$$  \hspace{1cm} (16)

3. Exothermic or Endothermic Heats Observed above the Melting Temperature $T_m$

3.1. Exothermic Enthalpy Delivered at 688 K in Al$_{88}$Ni$_{10}$Y$_2$ for $T_m = 602$ K

We follow data of ref. [41]. The glass transition occurs at $T_g = 380$ K, and the melting temperature at $T_m = 602$ K. In Figure 1, an annealing of 60 s at $T_a = 401, 427, and 525$ K increases the fraction $V_f$ of Al-fcc precipitates up to 0.42 and decreases the volume of the amorphous phase without changing the enthalpy recovery at 688 K measured at 0.67 K/s.

![Figure 1](image_url).

Figure 1. DSC curves measured at 0.67 K/s of an Al$_{88}$Ni$_{10}$Y$_2$ amorphous alloy aged for 60 s at different $T_a$. Reprinted from ref. [42], Figure 4.
3.2. Exothermic Enthalpy Delivered at $T_H = 1622\, K$ in $(Fe_{71.2}B_{24}Y_{4.8})_{96}Nb_4$

We follow data of ref. [42]. The glass transition occurs at $T_g = 963\, K$ and the melting temperature at $T_m = 1410\, K$. An enthalpy recovery occurs at 1622 K (Figure 2).

![Figure 2](image)

Figure 2. (a) High-temperature DSC trace at 0.33 K/s of the master alloy and (b) the enlarged version after melting. Reprinted with permission from ref. [42], Figure 7. Copyright 2014 Springer.

3.3. Exothermic Enthalpy Delivered at 1835 K in $Ni_{77.5}B_{22.5}$

We follow data of ref. [24]. The glass transition occurs at $T_g = 690\, K$ and the melting temperature at $T_m = 1361\, K$. The enthalpy recovery temperature is equal to 1835 K.

Deep transformations of eutectic liquid state are observed in Figure 3 by slow heating and aging above the melting temperature which are attributed to the formation of microdomains of 10–100 nm enriched with one of the components with prolonged relaxation time. These microdomains have an influence on the structure and properties of rapidly quenched liquid alloys [24,25]. The enthalpy recovery temperature is here the highest temperature of liquid transformation leading to its homogeneous state. A cooling from 1950 K gives rise to a homogeneous liquid leading to supercooling below $T_m = 1361\, K$.

![Figure 3](image)

Figure 3. Temperature dependence of the density $d$ of Ni-22.5% B melt at slow heating after melting and time exposition for 5–20 h (●), subsequent cooling (○), and the second heating after crystallization of the sample and repeated melting (△). The arrows show the “critical” temperatures at which the density instability is observed. Reprinted with permission from ref. [24], Copyright 1997 Elsevier.
3.4. Exothermic Enthalpy Delivered at 1356 K in Cu$_{47.5}$Zr$_{45.1}$Al$_{7.4}$

We follow data of ref. [43]. The glass transition occurs at $T_g = 690$ K and the melting temperature at $T_m = 1170$ K. An enthalpy recovery occurs at 1356 K (Figure 4).

![Figure 4](image_url)

**Figure 4.** Multiple DTA measurements (0.333 K/s) of Cu$_{47.5}$ alloy. The first up- and down-scan cycle is well below 1350 K and the last two cycles reach 1473 K. A remarkable exothermic reaction observed at the temperature above 1350 K in the second up-scan curve is marked by a gray dashed circle. Reprinted with permission from ref. [43], Figure 9b, Copyright 2020 Elsevier.

3.5. Endothermic Enthalpy Recovered at 1453–1475 K in a Silicate Liquid

We follow data of ref. [44]. The composition was (49.3SiO$_2$, 15.6Al$_2$O$_3$, 1.8TiO$_2$, 11.7FeO, 10.4CaO, 6.6MgO, 3.9Na$_2$O, and 0.7K$_2$O (wt%)). The glass transition occurred at $T_g = 908$ K and the melting temperature at $T_m = 1313$ K. The exothermic latent heat occurred at 1173 K and the amorphous fraction decline with the cycle number from 573 to 1523 K. The melting extended up to 1475 K in Figure 5, and the crystallization temperature $T_m$ occurred at 1313 K in Figure 6. The melting enthalpy recovered between $T_m$ and $T_{n+}$ was the same all along the cycles from 2 to 21.

Figure 6 shows that $T_m = 1313$ K. The transition at $T_{n+}$ during continuous cooling at 20 K/mn was no longer sharp and did not have a first-order character. Crystallization occurred at the melting temperature without undercooling, showing that the nuclei were growing between $T_{n+}$ and $T_m$ because they were formed above $T_m$ by homogenous nucleation accompanied by an enthalpy increase. Phase 3 disappeared above $T_{n+}$ and $\Delta \varepsilon_{lg} = 0$. Crystallization was sharper and sharper during cycling from temperatures higher than $T_{n+}$, showing that the short-range order was enhanced. The enthalpy coefficient $\Delta \varepsilon_{lg}$ of phase 3 grew by cooling below $T_{n+}$. 
3.6. Endothermic Enthalpy Recovered at 1114 K in Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5} (Vit1)

We follow data of ref. [45]. The glass transition occurred at $T_g = 625$ K and the melting temperatures at $T_{sol} = 965$ K and $T_{liq} = 1057$ K (Figure 7). There was an endothermic enthalpy at $T = 1114$ K. The heat capacity jump at $T_g$ was $\Delta C_p (T_g) = 21.6$ J/K/g-atom. A heat capacity peak of superheated liquid after supercooling was observed during heating around $T = 1114$ K, accompanied by an endothermic latent heat of about 1100 J/mole. Another transition, observed by viscosity measurements, occurred at 1225 K by heating and subsequent cooling, showing that the liquid became homogeneous above this temperature [46].

Figure 5. The repeated DSC up-scanning to 1250 °C ($T_{liq} + 70$ °C) at 0.333 K/s. The numerals next to the graphs represent the order of the DSC up-scans. The measurements are performed in argon at the heating rate 20 °C/min. Reprinted with permission from ref. [44], Figure 2, Copyright 2004 Elsevier.

Figure 6. The repeated DSC down-scanning from 1250 °C ($T_{liq} + 70$ °C) at 0.333 K/s. The numerals next to the graphs represent the order of the DSC down-scans. The measurements are performed in argon at the cooling rate 20 °C/min. Reprinted with permission from ref. [44], Copyright Elsevier.
Structural changes corresponding to these anomalies were still observed with in-situ synchrotron X-ray-scattering experiments in a contactless environment using an electrostatic levitator (ESL). There was an endothermic liquid–liquid transition at 1114 K during heating reinforced by the symmetrical observation of an exothermic latent heat regarding \( T_m = 965 \) K and an exothermic structural change around 816 K by supercooling.

3.7. Endothermic Enthalpy Recovered at 980–1000 K for \( T_m = 876–881 \) K in PdNiP Liquid Alloys

The heat capacities of several PdNiP alloys measured at 20 K/min are represented in Figure 8. The melting temperatures were slowly varying with composition around 880 K and an enthalpy recovery temperature was still observed around 990 K in many liquid alloys. The theoretical predictions for these liquid alloys were limited to the case of Pd\(_{42.5}\)Ni\(_{42.5}\)P\(_{15}\) [21] presented in Sections 6.1 and 7.1.

![Figure 7](image1.png)

**Figure 7.** \( C_p \) measured upon heating at 30 K/min for the amorphous sample (upper) and once-melted crystallized sample (lower) (vertically shifted for clarity). Reprinted from ref. [45], Figure 1b.

![Figure 8](image2.png)

**Figure 8.** DSC data during heating for Pd-Ni-P metallic glasses. The heating rate is 20 K/min. The curves have been shifted vertically for clarity. Reprinted from ref. [47], Figure S3.
4. Predictions of Enthalpy Recovery Temperatures at $T_{n^+} > T_m$

Equations (10)–(15) were used to calculate the enthalpy coefficients of fragile Liquids 1, 2, and 3 in Section 4.1, Section 4.2, Section 4.4, Section 4.5, and Section 4.6. Liquid Ni$_{77.5}$B$_{22.5}$ in 4.3 being strong, the enthalpy coefficients $\varepsilon_{ls0}$ and $\varepsilon_{gs0}$ were calculated with (9) for $\theta_{n^-} = \theta_g$, $\theta_{g2} = 1$, and $\theta_{0m2} = 4/9$.

4.1. Exothermic Enthalpy Delivered at $T_{n^+} = 688$ K in Al$_{88}$Ni$_{10}$Y$_2$

We follow data of ref. [41]. The enthalpy coefficients of this fragile glass-forming melt were calculated with $T_g = 380$ K and $T_m = 602$ K:

- Liquid 1: $\varepsilon_{ls}(\theta) = 1.63123 \left(1 - \theta^2 / 0.26736\right)$ (17)
- Liquid 2: $\varepsilon_{gs}(\theta) = 1.44694 \left(1 - \theta^2 / 0.3557\right)$ (18)
- Liquid 3: $\Delta \varepsilon_{lg}(\theta) = 0.18439 - 2.05237 \times \theta^2$ (19)

The temperature $T_{n^+} = 688$ K was deduced from $\theta_{n^+} = \Delta \varepsilon_{lg}(\theta_{n^+}) = 0.14287$ [48]. In Figure 1, an exothermic enthalpy peak is observed at 688 K for all samples at 0.67 K/s.

4.2. Exothermic Enthalpy Delivered at $T_{n^+} = 1622$ K in (Fe$_{71.2}$B$_{24}$Y$_{4.8}$)$_{96}$Nb$_4$

We follow data of ref. [42]. The enthalpy coefficients of this fragile glass-forming melt were calculated with $T_g = 963$ K and $T_m = 1410$ K [48]:

- Liquid 1: $\varepsilon_{ls}(\theta) = 1.61206 \left(1 - \theta^2 / 0.27795\right)$ (20)
- Liquid 2: $\varepsilon_{gs}(\theta) = 1.41609 \left(1 - \theta^2 / 0.36676\right)$ (21)
- Liquid 3: $\Delta \varepsilon_{lg}(\theta) = 0.19397 - 1.93329 \times \theta^2$ (22)

The temperature $T_{n^+} = 1622$ K was deduced from $\theta_{n^+} = \Delta \varepsilon_{lg}(\theta_{n^+}) = 0.1503$ [48].

4.3. Exothermic Enthalpy Delivered at $T_{n^+} = 1835$ K in Ni$_{77.5}$B$_{22.5}$

We follow data of ref. [24]. The enthalpy coefficients of this strong glass-forming melt were calculated with $T_g = 690$ K and $T_m = 1410$ K [48]:

- Liquid 1: $\varepsilon_{ls}(\theta) = 1.09891 \left(1 - \theta^2 / 0.44444\right)$, (23)
- Liquid 2: $\varepsilon_{gs}(\theta) = 0.51347 \left(1 - \theta^2\right)$ (24)
- Liquid 3: $\Delta \varepsilon_{lg}(\theta) = 0.58553 - 1.958 \times \theta^2$ (25)

The temperature $T_{n^+} = 1835$ K was deduced from $\theta_{n^+} = \Delta \varepsilon_{lg}(\theta_{n^+}) = 0.34808$ [48] in agreement with Figure 3.

4.4. Exothermic Enthalpy Delivered at $T_{n^+} = 1356$ K in Cu$_{47.5}$Zr$_{45.1}$Al$_{7.4}$

We follow data of ref. [43]. The enthalpy coefficients of this fragile glass-forming melt were calculated from $T_g = 690$ K and $T_m = 1170$ K:

- Liquid 1: $\varepsilon_{ls}(\theta) = 1.5906 \left(1 - \theta^2 / 0.28942\right)$ (26)
- Liquid 2: $\varepsilon_{gs}(\theta) = 1.3859 \left(1 - \theta^2 / 0.37826\right)$ (27)
- Liquid 3: $\varepsilon_{lg}(\theta) = 0.2047 - 1.83194 \times \theta^2$ (28)

The temperature $T_{n^+} = 1356$ K and the recovered enthalpy coefficient $\Delta \varepsilon_{lg}$ were deduced from $\theta_{n^+} = \Delta \varepsilon_{lg}(\theta_{n^+}) = 0.1586$ [48] in agreement with Figure 4. The enthalpy
coefficient $\Delta \varepsilon_{lg}$ reappeared by homogeneous nucleation below $T_{n+}$ because $\varepsilon_{gs}(\theta_{n+})$ was weaker than $\varepsilon_{ls}(\theta_{n+})$ and liquid 1 enthalpy decreased toward that of liquid 2 at slow cooling.

4.5. Endothermic Enthalpy Recovered at $T_{n+} = 1470$ K in a Silicate Liquid

We follow data of ref. [44]. The enthalpy coefficients of this fragile glass-forming melt were calculated with $T_g = 908$ K and $T_m = 1313$ K:

Liquid 1: $\varepsilon_{ls}(\theta) = 1.69155 \left(1 - \frac{\theta^2}{0.23189}\right)$ (29)

Liquid 2: $\varepsilon_{gs}(\theta) = 1.53732 \left(1 - \frac{\theta^2}{0.31613}\right)$ (30)

Phase 3: $\Delta \varepsilon_{lg}(\theta) = 0.15473 - 2.4315 \times \theta^2$ (31)

The temperature $T_{n+} = 1470$ K was deduced from $\theta_{n+} = \Delta \varepsilon_{lg}(\theta_{n+}) = 0.1195$ [48] in agreement with Figure 5.

4.6. Endothermic Enthalpy Recovered at $T_{n+} = 1114$ K in Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ (Vit1)

We follow data of ref. [45]. The enthalpy coefficients of this fragile glass-forming melt were calculated with $T_g = 625$ K and $T_m = 965$ K [35]:

$\varepsilon_{ls} = 1.70651 \times \left(1 - \frac{\theta^2}{0.2226}\right)$ (32)

$\varepsilon_{gs} = 1.4715 \times \left(1 - \frac{\theta^2}{0.34564}\right)$ (33)

$\Delta \varepsilon_{lg} = 0.23501 - 3.409 \times \theta^2$. (34)

The temperature $T_{n+} = 1114$ K was deduced from $\theta_{n+} = \Delta \varepsilon_{lg}(\theta_{n+}) = 0.15407$ [48] in agreement with Figure 6. The observed double transition was the consequence of the presence in the melt of nuclei, all having the same Gibbs free energy, leading to a homogenous nucleation at 818 and 1114 K as consequence of the quadratic equation of $\Delta \varepsilon_{lg}(\theta_{n+}) = \theta_{n+}$. The ordered liquid was rebuilt at $T_{n+} = 818$ K during cooling from 1350 K with the formation in the no-man’s land of new superclusters, building a vitreous solid phase at $T_g$ resulting of the bond number divergence. The hysteresis of viscosity disappeared at about 1225 K when the liquid is homogeneous [46]. A “colloidal” state was melted above the temperature of viscosity or density branching observed during cooling after heating [24,26,27,46]. Equation (35) was used to calculate the reduced temperature $\theta_{n+}$ of glass-forming melt with a glass transition at $\theta_g$ and obeying (11) with $a = 1$ [48]:

$\theta_{n+} = -0.38742 \times \theta_g$ (35)

The liquidus melting temperature $T_{liq} = 1057.5$ K was deduced from Equation (35) with $T_g = 625$ K and $T_{n+} = 1225$ K in perfect agreement with the experimental observation of liquidus presented in Figure 7. This finding of a second transition above $T_{n+}$ agreed with the first-order liquid–liquid transitions observed above $T_{n+}$ in Pd$_{42.5}$Ni$_{42.5}$P$_{15}$ and La$_{50}$Al$_{35}$Ni$_{15}$.

5. Three Liquid States above the Melting Temperature

The exothermic and endothermic transitions at $T_{n+}$ led to a liquid above $T_{n+}$ with an enthalpy coefficient $\Delta \varepsilon_{lg} = 0$. Two other liquid states existed at $T_m$ with enthalpy coefficients equal to $\pm \Delta \varepsilon_{lg}$. The melting temperature $T_m$ was chosen equal to $T_{solidus}$ in Figure 9. The enthalpy coefficients ($\pm \Delta \varepsilon_{lg}$), defined by (15) and applied to Pd$_{42.5}$Ni$_{42.5}$P$_{15}$ in Figure 9 and in Section 7.1, were related to the enthalpy decrease and increase with temperature of these two quenched liquid states toward that of homogeneous liquid.
The homogenous liquid can be quenched along q2 ($\Delta \epsilon_{lg0} = 0$) in Figure 9 from above the temperature where the liquid became homogeneous, down to temperatures much weaker than $T_g$ [49–51]. An enthalpy relaxation at low heating rate, equal to ($-\Delta \epsilon_{lg0} \times \Delta H_m$), built the bonds of phase 3 and led by heating to the temperature where $\Delta \epsilon_{lg} = 0$ [35]. This slow heating through $T_g$ broke the bonds and the liquid enthalpy increases up to ($+\Delta \epsilon_{lg0} \times \Delta H_m$) at $T_m$, producing an exothermic enthalpy at $T_{n+}$. These phenomena are observed in Figures 1–4.

With a much higher heating rate, the enthalpy of bonds, building phase 3, did not have the time to relax below $T_g$, and phase 3 was not formed along the thermal path below $T_g$ and the latent heat at $T_{n+}$ was not observed for Pd$_{42.5}$Ni$_{42.5}$P$_{15}$ at 100 K/s, as shown in Figure 10 [21]. The liquid being frozen below $T_g$ with $\Delta \epsilon_{lg} = 0$ gave rise to an endothermic enthalpy at $T_g$ due to bond breaking and the liquid returned to a homogenous state with $\Delta \epsilon_{lg0} = 0$ above $T_{n+}$ [10–12].

A quench along q1 in Figure 9 from $T_m < T < T_{n+}$ with a liquid enthalpy ($+\Delta \epsilon_{lg0} \times \Delta H_m$) at $T_m$ led to an amorphous phase with an enthalpy excess ($+\Delta \epsilon_{lg0} \times \Delta H_m$). Phase 3 bonds were built during reheating and they decreased, at a low heating rate, the enthalpy coefficient from ($+\Delta \epsilon_{lg0}$) below $T_g$ to ($-\Delta \epsilon_{lg0}$) at $T_m$, leading to an endothermic latent heat at $T_{n+}$ corresponding to crystallized nuclei melting at $T_{n+}$.

Starting heating at a very low heating rate from any liquid state led to crystallization and to a liquid enthalpy equal to ($-\Delta \epsilon_{lg0} \times \Delta H_m$) at $T_m$.

A quench from $T_m < T < T_{n+}$ along q3 led to the enthalpy of phase 3 with crystallized nuclei being the skeleton of this phase after percolation at $T_g$, as shown for plastic crystals. A slow cooling led to crystallization at $T_m$ without undercooling [19].

The endothermic and exothermic characters of the transition at $T_{n+}$ were imposed by the initial value of the liquid enthalpy after quenching and by cooling and heating rates.

Homogeneous nucleation in the liquid was expected to depend on the time of aging in the range of temperatures below and close to the homogenization temperature. The first-order liquid–liquid transitions in Pd$_{42.5}$Ni$_{42.5}$P$_{15}$ and La$_{30}$Al$_{35}$Ni$_{15}$ studied by [20,21] combined with our non-classical model of homogeneous nucleation shed light on these new phenomena.

6. First-Order Liquid–Liquid Transitions Observed in Pd$_{42.5}$Ni$_{42.5}$P$_{15}$, La$_{30}$Al$_{35}$Ni$_{15}$, and Fe$_2$B

We follow data of ref. [21] for Pd$_{42.5}$Ni$_{42.5}$P$_{15}$, of ref. [20] for La$_{30}$Al$_{35}$Ni$_{15}$ and of ref. [24] for Fe$_2$B.

6.1. Pd$_{42.5}$Ni$_{42.5}$P$_{15}$

6.1.1. Fast Differential Scanning Calorimetry at 100 K/s

The fast differential scanning calorimetry (FDSC) heating curve at 100 K/s represented in Figure 10 and reproduced from [21] was used to determine the solidus and liquidus
temperatures $T_{\text{sol}} = 876$ and $T_{\text{liq}} = 926.5$ K. A first-order liquid–liquid transition was observed at $T_{\text{LL}} = 1063$ K. The sample was previously cooled from 1073 K at 40,000 K/s down to room temperature and reheated up to 1073 K, which was a temperature higher than the first-order transition observed at $T_{\text{LL}}$.

![Figure 10](image1.png)

**Figure 10.** DSC with heating rate of 100 K/s. A typical FDSC heating curve of the sample obtained from $T_q = 1073$ K and $q^- = 40,000$ K/s. The enthalpy of crystallization is denoted as $\Delta H$. The inset shows the temperature protocol of the FDSC experiments. Temperatures $T_{\text{sol}}$, $T_{\text{liq}}$, and $T_{\text{LL}}$ added. Reprinted with permission from ref. [21], Figure 3a, Copyright 2021 Elsevier.

### 6.1.2. Melting Transition Observed at 993 K above the Solidus Temperature $T_{\text{sol}} = 876$ K of Pd$_{42.5}$Ni$_{42.5}$P$_{15}$

The samples were quenched from $T_q$ to room temperature at a cooling rate of $q^- = 40,000$ K/s and reheated at 100 K/s up to $T_q$, as shown in Figure 11b [21]. There was no nucleation when cooling started from 1073 K for $q > 70$ K/s, while crystallization occurred for $q < 7000$ K/s when cooling started from 1023 K as shown in Figure 11a. The area of the crystallization peak occurring around $T = 770$ K in Figure 10 was plotted versus $T_q$ in Figure 11b. The temperature $T = 993$ K was viewed by the authors as a liquidus transition which was, in fact, equal to 926.5 K, as shown in Figure 9.

![Figure 11](image2.png)

**Figure 11.** The content of amorphous phase as a function of cooling rate $q^-$ of the samples obtained from $T_q = 1073$ and 1023 K, respectively (a). The crystallized fraction characterized by $\Delta H$ is evaluated by FDSC as shown in Figure 10b. Area of the second exothermic peak $\Delta H$ as a function of $T_q$ as shown in Figure 10. (b) Area of the exothermic peak $\Delta H$ as a function of $T_q$ with a cooling rate of 40,000 K/s. Reprinted with permission from ref. [21], Figure 3b and Figure S1, Copyright 2021 Elsevier.
6.1.3. First-Order Transition Observed by $^{31}$P Nuclear Magnetic Resonance (NMR)

$^{31}$P NMR was used to characterize the LLT at $T_{LL} = 1063$ K above $T_{n+} = 993$ K. The liquid alloy was first heated to 1293 K for homogenization during 30 min, and then cooled step by step to 1043 K. NMR spectra were taken isothermally after equilibrating the liquid at 1293 K at each step. The Knight shift ($K_s$) was determined by the ensemble average of local magnetic field around $^{31}$P nuclei, sensitive to the changes in structure, plotted in Figure 12 as a function of temperature [21]. ($K_s$) varied linearly above 1063 K with a slope increase of 1.76 ppm/K below 1063 K, indicating a change in the P-centered local structures at this temperature. This change was viewed as a first-order liquid–liquid transition (LLT) analogous to that observed in La$_{50}$Al$_{35}$Ni$_{15}$ where a second change of $K_s$ in this new liquid state was observed at lower temperatures attributed to the hysteresis of the transition [20].

Figure 12. The changes of the Knight shift $K_s$ at different undercooled temperatures $T_{iso}$ after quenching the melt from 1173 K. The solid and open symbols represent the initial and equilibrium $K_s$, respectively. Reprinted with permission from ref. [21], Figure 1c, Copyright 2021 Elsevier.

6.2. La$_{50}$Al$_{35}$Ni$_{15}$

This melt was characterized by $T_g = 528$ K, $T_{sol} = 877.6$ K, and $T_{liq} = 892$ K, as shown in Figure 13 [20] Figure S1). A second liquidus temperature was found at 950 K. The temperature $T_{LL}$, observed at 1033 K by measuring the $^{27}$Al Knight shift by RMN, is viewed as a first-order LLT in Figure 14. A phenomenon analogous to hysteresis led to a second transition at 1013 K.

Figure 13. DSC trace of as-cast La$_{50}$Al$_{35}$Ni$_{15}$ BMG. The DSC curve obtained at a heating rate of 10 K/min. Liquidus temperature ($T_{liq}$) indicated by red arrows. The two liquidus temperatures ($T_{n+}$) and solidus temperature ($T_{sol}$) are added. Reprinted from ref. [20], Figure S1.
First-order transition occurs at $T_{si} = 1915$ K in Figure 15 with a melting temperature of 1662 K [24].

6.3. Fe$_2$B

The vitreous state of this compound was obtained by mechanical alloying [52]. The first-order transition occurs at $T_{ll} = 1915$ K in Figure 15 with a melting temperature of 1662 K [24].

Figure 15. Temperature dependence of the density $d$ of Fe-26.4 at %B and Fe-33.3 at %B melts at heating after melting (•) and subsequent cooling (○). Arrow shows the anomaly linked with structural transformation in a liquid compound. Reprinted with permission from ref. [24], Figure 8, Copyright 1997 Elsevier.

7. Predictions of First-Order Transition Temperatures by Homogenous Nucleation in Pd$_{42.5}$Ni$_{42.5}$P$_{15}$, La$_{50}$Al$_{35}$Ni$_{15}$ and Fe$_2$B Melts

These first-order transitions were observed at $T_{ll}$ at very low cooling rates or by isothermal annealing between the melting temperature and $T_{ll}$. The homogeneous liquid state characterized by $\Delta \epsilon_{lgt} = 0$ was stable during cooling in Figure 3 while the first-order transitions were reversible in Figure 15. The two melting temperatures $T_{sol}$ and $T_{liq}$ of non-congruent materials led to two nucleation temperatures $T_{n}$. 
7.1. Predictions of Transitions in Pd_{42.5}Ni_{42.5}P_{15} Melt

The temperature 993 K in Figure 11b was viewed by [21] as a liquidus temperature which was, in fact, equal to 926.5 K, as shown in Figure 10. The reduction of the enthalpy recovered by crystallization at 770 K occurred for T_q < 993 K, as shown in Figure 11b. The crystallization enthalpy at 770 K was continuously reduced without exothermic enthalpy jump equal 0.13357 \times 197 = 26 in Figure 11b at 993 K. The mean-range order accompanied by exothermic enthalpy progressively reappeared by homogeneous nucleation in the liquid heated during 30 s at each temperature T_q and was completely formed at T_{liq} = 926.5 K because the enthalpy decrease was equal to \(-13.4\%\) at this temperature. The residual configurons melted at T_{n^+} = 993 K using (35) (\theta_{n^+} = \Delta \epsilon_{lg}(\theta_{n^+}) = 0.13357), T_m = 876 K, and T_g = 574 K. This value of T_g agreed with measurements of heat capacity of melts with similar compositions [47]. The enthalpy coefficients of Pd_{42.5}Ni_{42.5}P_{15} for the liquidus and solidus liquid states were given in Equations (36–38) using Equations (10–16):

For T_{sol} = 876 K and T_g = 574 K

\[
\text{Liquid 1 : } \epsilon_{ls}(\theta) = 1.6552\left(1 - \theta^2/0.25362\right)
\]
\[
\text{Liquid 2 : } \epsilon_{gs}(\theta) = 1.4828\left(1 - \theta^2/0.34081\right)
\]
\[
\text{Phase 3 : } \Delta \epsilon_{lg}(\theta) = 0.17237 - 2.1755 \times \theta^2
\]

For T_{Liq} = 926.45 K and T_g = 574 K

\[
\text{Liquid 1 : } \epsilon_{ls}(\theta) = 1.61957\left(1 - \theta^2/0.27384\right)
\]
\[
\text{Liquid 2 : } \epsilon_{gs}(\theta) = 1.42935\left(1 - \theta^2/0.36251\right)
\]
\[
\text{Phase 3 : } \Delta \epsilon_{lg}(\theta) = 0.19022 - 1.97146 \times \theta^2
\]

Applying Equation (35) led to T_{n^+} = T_{LL} = 1063 K in perfect agreement with Figure 12. From our analysis, a second change of K_s occurred by homogeneous nucleation in Pd_{42.5}Ni_{42.5}P_{15} at T_{n^+} = 993 K. This transition was not only due to the hysteresis of a first-order transition because there were two homogeneous nucleation temperatures as shown in Figure 12. This point was still confirmed in 7.2 devoted to La_{80}Al_{35}Ni_{15}, where the changes of K_a occurred for two values of T_{n^+} because there were, in these non-congruent liquid compounds, two solid–liquid transitions characterized by solidus and liquidus temperatures.

The temperature T_{n^+} = T_{LL} = 1063 K corresponded to the temperature of homogeneous nucleation of colloids containing critical numbers n_c of atoms with n_c given by Equation (42) (see [9], Equation (48)):

\[
n_c = \frac{8N_A k_B \left(1 + \Delta \epsilon_{lg}\right)^3}{27 \Delta S_m \left(\Delta \epsilon_{lg}\right)^3} \ln(K)
\]

where N_A is the Avogadro number, k_B the Boltzmann constant, \Delta S_m the melting entropy, and \ln K \equiv 90 [5]. With \Delta \epsilon_{lg} = 0.13356 and \Delta S_m = 8.76 J/g-atom [47], n_c = 15522 at the temperature T_{n^+} = 993 K. With \Delta \epsilon_{lg} = 0.14739 and \Delta S_m = 8.76 J/g-atom, n_c = 11977 at the temperature T_{n^+} = 1063 K. Critical numbers n_c, still larger, were observed in Pb-Bi liquid alloys below the temperature of liquid homogenization [27]. The number of atoms inside an elementary superatom in the homogenous liquid above 1063 K was equal to 135, with \Delta \epsilon_{lg}(\theta_{n^+}) replaced in (42) by \epsilon_{gs}(\theta_{n^+}) = 1.40526 in (42) using Equations (39) and (40). The homogenous nucleation time \tau (s) for temperatures 1043 < T < 1063 K was following Equation (43) (see Figure 1d in ref. [21]):

\[
\tau (s) = 5.9 \times 10^{-3} \left(\frac{1063}{T} - 1\right)^{2.18}
\]

which led by extrapolation to \tau \equiv 1.9 s at T_{n^+} = 993 K.
There was no growth nucleus inducing crystallization after quenching from the temperature \( T = 1073 \) K which was higher than \( T_{\text{ll}} = 1063 \) K as shown in Figure 11a [21]. New growth nuclei were added when the melt was quenched from 1023 K, a temperature higher than \( T_{n+} = 993 \) K and much higher than \( T_{\text{sol}} \). Consequently, new denser nuclei growing from the colloidal state were added by homogeneous nucleation at 1023 K above 993 K. The transition at 993 K after cooling from 1073 K was due to the internal and external bond formation between colloids below 1063 K [18]. This observation agreed with the growth of \( n_c \) from 11977 to 15522 between 1063 and 993 K. The transitions observed by NMR below 1063 K involved all \(^{31}P\) atoms and corresponded to the colloid formation through the relaxation time decrease [23]. The first-order character of this transition was observed at each step of isothermal annealing below 1063 K. The breaking of bonds inside and outside colloids occurred at the lowest temperature \( T_{n+} \) during heating [18], while at the highest \( T_{n+} \), a transition from colloidal state to a new homogeneous state made of elementary superatoms only organized by short-range order appeared.

The enthalpy coefficients (\( -\Delta\varepsilon_{\text{lg}} \)) of phase 3 equal to those of configurons are represented in Figure 16 as a function of the temperature \( T \) (K) for \( T_{\text{sol}} \) and \( T_{\text{liq}} \) using Equations (38) and (41). The crystallization temperature occurred at the reentrant formation temperature of ultrastable glass with its enthalpy equal to \( -\Delta\varepsilon_{\text{lg}} \). This nucleation temperature opened the door to crystallization [19].

![Figure 16](image)

**Figure 16.** Enthalpy coefficients of liquidus and solidus melts versus \( T \) (K). \( T_{\text{liq}} = 926.5 \) K, \( T_{n+} = 1063 \) K, \( T_{\text{sol}} = 876 \) K, and its \( T_{n+} = 993 \) K. Crystallization at the nucleation temperature \( T_3 = 748.4 \) K of phase 3 in solidus melt instead of \( T_3 = 774.2 \) K in liquidus melt. In the liquidus melt, \( T_{\text{ll}} = T_{n+} = 1063 \) K.

### 7.2. Predictions of First-Order Transitions in La\(_{50}\)Al\(_{35}\)Ni\(_{15}\) Glass-Forming Melt

We follow data of ref. [20]. The phase 3 enthalpy coefficients of La\(_{50}\)Al\(_{35}\)Ni\(_{15}\) for the liquidus and solidus liquids were given in Equations (44)-(49) for \( T_{\text{sol}} = 877.6 \) K, \( T_{\text{liq}} = 892 \) K, and \( T_g = 528 \) K, and are represented in Figure 17.

![Figure 17](image)

**Figure 17.** La\(_{50}\)Al\(_{35}\)Ni\(_{15}\) enthalpy coefficients of liquidus and solidus melts. \( T_{\text{sol}} = 877.6 \) K; \( T_{n+} = 1013 \) K; \( T_{\text{liq}} = 892 \) K; \( T_{\text{ll}} = T_{n+} = 1033 \) K. The enthalpy coefficients of ultrastable phase 3 are \((-0.19918)\) for the solidus and \((-0.20404)\) for the liquidus. The two melts have the same \( T_g = 574 \) K.
For $T_{\text{Liq}} = 892$ and $T_g = 528$ K:

- Liquid 1: $\epsilon_{\text{liq}}(\theta) = 1.66143 \left( 1 - \frac{\theta^2}{0.25000} \right)$

- Liquid 2: $\epsilon_{\text{gs}}(\theta) = 1.42935 \left( 1 - \frac{\theta^2}{0.33679} \right)$

- Phase 3: $\Delta\epsilon_{\text{lg}}(\theta) = 0.20404 - 2.2516 \times \theta^2$

For $T_{\text{sol}} = 877.6$ and $T_g = 528$ K:

- Liquid 1: $\epsilon_{\text{liq}}(\theta) = 1.60164 \left( 1 - \frac{\theta^2}{0.28357} \right)$

- Liquid 2: $\epsilon_{\text{gs}}(\theta) = 1.40246 \left( 1 - \frac{\theta^2}{0.37246} \right)$

- Phase 3: $\Delta\epsilon_{\text{lg}}(\theta) = 0.19218 - 1.88273 \times \theta^2$

7.3. Predictions of Glass Transition Temperature of Fe$_2$B Melt

The enthalpy coefficients of the strong liquid Fe$_2$B were calculated with Equations (9) and (35), $T_m = 1662$ K and $T_{n^+} = T_{\text{LL}} = 1915$ K, given in Equations (50)–(52). Phase 3 is represented in Figure 18.

![Figure 18. Enthalpy coefficient $\Delta\epsilon_{\text{lg}}(T)$ of Fe$_2$B Phase 3 and configurons. $T_3 = 903$ K, $T_g = 1125.7$ K, $T_m = 1662$ K, $T_{n^+} = T_{\text{LL}} = 1915$ K.](image)

For $T_m = 1662$ K and $T_{n^+} = T_{\text{LL}} = 1915$ K, $T_g = 1125.7$ K:

- Liquid 1: $\epsilon_{\text{liq}}(\theta) = 1.60164 \left( 1 - \theta^2 \times 2.25 \right)$

- Liquid 2: $\epsilon_{\text{gs}}(\theta) = 1.1519 \left( 1 - \theta^2 \right)$

- Phase 3: $\Delta\epsilon_{\text{lg}}(\theta) = 0.19579 - 1.8804 \times \theta^2$

7.4. One Liquid–Liquid Transition at $T_{n^+} = T_{\text{LL}}$ in Congruent Materials and Two in the Others

A first-order transition occurred at $T_{\text{LL}}$ due to the formation by cooling of colloidal state assembling elementary superatoms composed of tenths atoms bounded by short-range interactions, leading to colloids containing thousands of atoms. In the case of congruent materials, only one liquid–liquid transition was expected. The lowest and the highest temperatures $T_{n^+}$ were equal and $T_{n^+}$ is a first-order transition temperature equal to $T_{\text{LL}}$. This is the case for Fe$_2$B.

These colloids were similar atom clouds containing a magic atom number of atoms because they were melted by homogeneous nucleation instead of surface melting. They
had a maximum radius for which their Gibbs free energy was smaller or equal to that of the melt [53].

There were two liquid–liquid transitions above the solidus and liquidus temperatures \( T_{\text{sol}} \) and \( T_{\text{liq}} \) in non-congruent materials, leading to two temperatures \( T_{n+} \). The highest one was equal to \( T_{\text{LL}} \) and related to \( T_{\text{liq}} \). Above \( T_{\text{LL}} \), the liquid was homogeneous and atoms were only submitted to short-range order in tiny superatoms. The lowest \( (T_{n+}) \) was related to \( T_{\text{sol}} \) and was the temperature where coupling between elementary superatoms started during cooling and led to bond percolation at \( T_g \). The lowest one was a second-order phase transition where the residual configurons were melted during heating, involving 15% of the sample volume.

A melt was only rejuvenated above \( T_{n+} \) because all colloids and superatoms were disconnected.

8. Perspectives: Mpemba Effect and Bonding-Antibonding of Superatoms

8.1. Mpemba Effect and Its Inverse Relation to the Existence of Three Liquid States above the Melting Temperature

The Mpemba effect is described by a shorter time needed to crystallize a hot water system than to crystallize the same colder water system cooled down from initial lower temperatures [54]. This phenomenon was documented by Aristotle 2300 years ago [55]. The melting enthalpy of ice was \( \Delta H_m = 334 \text{ J/g} \) with a specific heat of \( 4.18 \text{ J/g} \). Starting from a hot homogenous water, the exothermic enthalpy of formation of mean-range order below \( T_{n+} = 295.3 \text{ K} \) (22.1 °C) [34] was progressively equal to \(-0.0818 \times 334 = -27.3 \text{ J/g} \) by homogenous nucleation during slow cooling through \( T_{n+} \). The value of \( T_{n+} \) in water was confirmed by numerical simulations of the melting temperature of an ultrathin layer of hexagonal ice [19,56–58]. The water enthalpy variation being equal to 92 J/g from 22.1 to 0 °C, the temperature of 0 °C was quickly attained by the hot system because of the recovery of exothermic enthalpy. The cold water had no more available exothermic enthalpy because the formation of mean range order was much older in this water. Cooling this liquid took much more time.

The latent heat, expected at \( T_{n+} = 22.1 \text{ °C} \), was not observed up to now, while Mpemba and Osborne observed this effect with a slow cooling rate of 0.01 K/s. The window of nucleation was very narrow in congruent materials because the temperature \( T_{n+} \) was unique instead of extending between the two \( T_{n+} \) temperatures of non-congruent substances as shown in Figure 13. At a too-high cooling rate, the liquid state, with \( \Delta \varepsilon_{\text{lg}} = 0 \), free of any growth nucleus, remained stable and showed undercooling. The homogeneous liquid state was stable when it escaped the formation of colloidal state at \( T_{n+} \). Figure 3 showed this phenomenon in Fe\(_{77.5}\)B\(_{22.5}\). On the contrary, the transition of Fe\(_2\)B at \( T_{n+} = 1915 \text{ K} \) had a first-order character (see Figure 15) Nucleus formation started from the colloidal state and was expected to be formed at a low cooling rate.

Using the theory of nonequilibrium thermodynamics, Lu and Raz predicted a similar anomalous behavior with heating using a three-state model that we had here for all melts [59]. A cold liquid, with an enthalpy equal to \(+\Delta \varepsilon_{\text{lg0}} \times \Delta H_m\), obtained after building bonds below \( T_g \), would develop an exothermic latent heat at \( T_{n+} \) during heating, while a warmer liquid with an enthalpy equal to \(-\Delta \varepsilon_{\text{lg0}} \times \Delta H_m\) would need an endothermic enthalpy to melt its mean-range order.

The Mpemba effect and its inverse effect can be extended to many systems [59,60] and we showed that these phenomena could exist in all melts. Moreover, we assumed that analogues of Mpemba effects should occur on vitrification of liquids so that glasses would be formed quicker out of hot melts compared with melts cooled down from lower temperatures. All these new events were observable because the transition at \( T_{n+} \) was a first-order transition in congruent materials [24].
8.2. Three Liquid States Associated with Bonding–Antibonding of Superatoms

In Figure 9, the enthalpy coefficient of phase 3 at $T_{n^+}$ was equal to three values $+\Delta\varepsilon_{lg}$, 0, and $-\Delta\varepsilon_{lg}$ depending on thermal history leading to three liquid states. The glass transitions occurred at the percolation threshold of superclusters, built by homogeneous nucleation, during the first cooling of liquids initially homogeneous. These superclusters survive in overheated colloids after their formation during the first cooling because they were melted at $T_{n^+}$ by homogeneous nucleation instead of surface melting at $T_m$. These entities were contained in colloids with a magic atom number [61]. Thus, they were melted at $T_{n^+}$ when their Gibbs free energy became equal to that of homogeneous liquid [53]. The endothermic and exothermic latent heats revealed the existence of two families of bound molecules which could be attributed to bonding and antibonding of colloids through elementary superatoms. This concept of bonding and antibonding is highly developed in bond chemistry to create new chemical structures. Bonding and antibonding of colloids could lead to higher and lower enthalpies. Two recent examples of research in this field were given [62,63]. The nature built these new superstructures in all overheated melts by homogeneous nucleation. The percolation of these superatoms led $T_g$ to a superstructure involving 3D space in 15% of atoms [18].

9. Conclusions

Our homogeneous nucleation models explained the formation of liquid phases above $T_g$ with mean-range order disappearing at a temperature $T_{n^+}$ much higher than the melting temperature. This transformation at $T_{n^+}$ was a first-order transition in congruent materials such as Fe$_2$B and was expected to be observable at a very low cooling rate or by homogeneous nucleation during isotherm annealing below $T_{n^+}$. There were two melting temperatures in non-congruent materials called solidus and liquidus temperatures, leading to two temperatures: $T_{n^+}$, starting with a unique glass transition temperature $T_g$. The first-order liquid–liquid transitions in Pd$_{42.5}$Ni$_{42.5}$P$_{15}$ and La$_{50}$Al$_{35}$Ni$_{15}$ observed with NMR at $T_{LL}=1063$ and 1033 K, respectively, occurred at the temperature $T_{n^+}$ corresponding to the liquidus temperature of these two alloys. The two other second-order phase transitions, occurring at $T_{n^+}=993$ and 1013 K respectively, were induced by the solidus temperatures.

The latent heats produced at $T_{n^+}$ were exothermic or endothermic. We attributed this phenomenon to the presence of three liquid states at $T_{n^+}$, with three enthalpy coefficients depending on the cooling rate and on the starting temperature of quenching. These enthalpies were equal to 0, $+\Delta H_m \times \Delta\varepsilon_{lg}$ ($T_{n^+}$), and $-\Delta H_m \times \Delta\varepsilon_{lg}$ in comparison with that of a homogeneous liquid equal to zero at high temperatures. These liquids, when quenched to temperatures much weaker than $T_g$, were characterized by their initial enthalpy at the solidus temperature. The liquid state enthalpy after quenching was $(-\Delta H_m \times \Delta\varepsilon_{lg0})$, or $(+\Delta H_m \times \Delta\varepsilon_{lg0})$, or 0 depending on its initial value before quenching and on the cooling and heating rates. The enthalpy increased from $-\Delta H_m \times \Delta\varepsilon_{lg0}$ and 0 up to $+\Delta H_m \times \Delta\varepsilon_{lg0}$ at $T_m$ with configuron melting. The enthalpy decreased from $+\Delta H_m \times \Delta\varepsilon_{lg0}$ and 0 to $-\Delta H_m \times \Delta\varepsilon_{lg0}$ at $T_m$, rebuilding the missing bonds. These phenomena were well described by the positive or negative variation $\pm \Delta H_m \times \Delta\varepsilon_{lg}$ ($T_{n^+}$), of enthalpies of bonds and configurons.

Our homogeneous nucleation model above $T_m$ still confirmed the formation of colloids between $T_{n^+}$ and $T_m$ and at slow cooling rate, the growth of cluster-bound colloids inducing crystallization. The temperature $T_{n^+}$, congruent materials being unique, was the temperature of homogenization of these melts. The highest temperature $T_{n^+}=T_{LL}$ observed in Pd$_{42.5}$Ni$_{42.5}$P$_{15}$ and La$_{50}$Al$_{35}$Ni$_{15}$ was a homogenization temperature of these non-congruent materials. All melts, containing atoms of different nature, were submitted to short-range order inside superatoms, being the elementary bricks building the ordered liquids and glasses.

These colloids and elementary superatoms could not be more precisely described because their magic atom number $n_m$ and the associated enthalpy depending on $n_m$ were unknown.
Colloids formed by homogeneous nucleation were superatoms containing magic atom numbers which were not totally melted above $T_m$ and were fully melted by homogenous nucleation instead of surface melting at the highest temperature $T_{n+}$. They contained a critical atom number $n_c$ defined by their Gibbs free energy equal or smaller than that of the homogeneous melt. They gave rise to new molecular entities by bonding and antibonding, as shown by the opposite values of their contribution to the enthalpy at $T_{n+}$. Superstructures of elementary superatoms grew during cooling down to their percolation temperature.

The Mpemba effect and its inverse were easily predicted from this description of materials melting, leading to three stable liquid states above the melting temperature and transitions between them. The transition at $T_{n+}$ may have been not only the temperature where the mean-range order disappeared, but also a first-order transition temperature between two liquid states.

**Author Contributions:** Conceptualization, R.F.T. and M.I.O.; methodology, R.F.T.; software, R.F.T.; validation, R.F.T. and M.I.O.; formal analysis, R.F.T.; investigation, R.F.T.; resources, R.F.T. and M.I.O.; data curation, R.F.T.; writing—original draft preparation, R.F.T.; writing—review and editing, R.F.T. and M.I.O.; visualization, R.F.T.; supervision, R.F.T. and M.I.O. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data underlying this article will be shared on reasonable request from the corresponding author.

**Acknowledgments:** Thanks to L.N.C.M.I., Grenoble Alpes University, Imperial College London.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. De Rango, P.; Lees, M.; Lejay, P.; Sulpice, A.; Tournier, R.; Ingold, M.; Germi, P.; Pernet, M. Texturing of magnetic materials at high temperature by solidification in a magnetic field. *Nature* 1991, 349, 770–772. [CrossRef]
2. Tournier, R.F.; Beaugnon, E. Texturing by cooling a metallic melt in a magnetic field. *Sci. Technol. Adv. Mater.* 2009, 10, 014501. [CrossRef]
3. Porcar, L.; De Rango, P.; Bourgault, D.; Tournier, R.F. Magnetic Texturing of High-Tc Superconductors; Gabovitch, A., Ed.; BoD-Books on demand: Norderstedt, Germany, 2012; p. 171.
4. Turnbull, D. Kinetics of solidification of supercooled liquid mercury. *J. Chem. Phys.* 1952, 20, 411. [CrossRef]
5. Vinet, P.; Magnusson, L.; Frederiksen, H.; Desré, P. Correlations between surface and interface energies with respect to crystal nucleation. *J. Colloid Interf. Sci.* 2002, 255, 363–374. [CrossRef]
6. Tournier, R.F. Presence of intrinsic growth nuclei in overheated and undercooled liquid elements. *Phys. B* 2007, 392, 79–91. [CrossRef]
7. Tournier, R.F. Influence of Fermi energy equalization on crystal nucleation in glass melts. *J. Alloys Comp.* 2009, 483, 94–96. [CrossRef]
8. Tournier, R.F. Thermodynamic origin of the vitreous transition. *Materials* 2011, 4, 869–892. [CrossRef]
9. Tournier, R.F. Fragile-to-fragile liquid transition at $T_g$ and stable-glass phase nucleation rate maximum at the Kauzmann temperature. *Phys. B* 2014, 454, 253–271. [CrossRef]
10. Wool, R.P. Twinkling fractal theory of the glass transition. *J. Polym. Sci. Part B Polym. Phys.* 2008, 46, 2765–2778. [CrossRef]
11. Wool, R.P.; Campanella, A. Twinkling fractal theory of the glass transition: Rate dependence and time-temperature superposition. *J. Polym. Sci. Part B Polym. Phys.* 2009, 47, 2578–2589. [CrossRef]
12. Stanziione, J.F., III; Strawhecker, K.E.; Wool, R.P. Observing the twinkling nature of the glass transition. *J. Non-Cryst. Sol.* 2011, 357, 311. [CrossRef]
13. Ojovan, M.I.; Travis, K.P.; Hand, R.J. Thermodynamic parameters of bonds in in glassy materials from viscosity temperature relationships. *J. Phys. Cond. Matter.* 2007, 19, 415107. [CrossRef] [PubMed]
14. Ojovan, M.I.; Lee, W.E. Connectivity and glass transition in disordered oxide systems. *J. Non-Cryst. Sol.* 2010, 356, 2534–2540. [CrossRef]
15. Ojovan, M.I. Ordering and connectivity changes at the glass-liquid transition. *J. Non-Cryst. Sol.* 2013, 382, 79. [CrossRef]
16. Ojovan, M.I. Louguine Luzgin, D.V. Revealing structural changes at glass transition via radial distribution functions. *J. Phys. Chem. B.* 2020, 124, 3186–3194. [CrossRef] [PubMed]
17. Sanditov, D.S.; Ojovan, M.I.; Darmaev, M.V. Glass transition criterion and plastic deformation of glass. Phys. B 2020, 582, 411914. [CrossRef]
18. Tournier, R.F.; Ojovan, M.I. Undercooled Phase Behind the Glass Phase with Superheated Medium-Range Order above Glass Transition Temperature. Phys. B 2021, 602, 412542. [CrossRef]
19. Tournier, R.F.; Ojovan, M.I. Dewetting temperatures of prefrzen and grated layers in ultrathin films viewed as melt-memory effects. Phys. B 2021, 611, 412796. [CrossRef]
20. Xu, W.; Sandor, M.T.; Yu, Y.; Ke, H.-B.; Zhang, H.-B.; Li, M.-Z.; Wang, M.-Z.; Liu, L.; Wu, Y. Evidence of liquid-liquid transition in glass-forming La$_2$Al$_3$Ni$_{15}$ melt above liquidus temperature. Nat. Commun. 2015, 6, 7696. [CrossRef]
21. Chen, E.-Y.; Peng, S.-X.; Peng, L.; Michiel, M.D.; Vaughan, G.B.M.; Yu, Y.; Yu, H.-B.; Ruta, B.; Wei, S.; Liu, L. Glass-forming ability correlated with the liquid-liquid transition in Pd$_{12.5}$Ni$_{12.5}$P$_{15}$ alloy. Scr. Mater. 2021, 193, 117–121. [CrossRef]
22. Tanaka, H. Liquid-liquid transition and polymorphism. J. Chem. Phys. 2020, 153, 130901. [CrossRef] [PubMed]
23. Popel, P.S.; Chikova, O.A.; Matveev, V.M. Metastable colloidal states of liquid metallic solutions. High Temp. Mater. Proc. 1995, 4, 219–233. [CrossRef]
24. Popel, P.S.; Sidorov, V.E. Microheterogeneity of liquid metallic solutions and its influence on the structure and properties of rapidly quenched alloys. Mater. Sci. Eng. 1997, A226-2289, 237–244. [CrossRef]
25. Dahlborg, U.; Calvo-Dahlborg, M.; Popel, P.S.; Sidorov, V.R. Structure and properties of some glass-forming liquid alloys. Eur. Phys. J. B 2000, 14, 639–648. [CrossRef]
26. Manov, V.; Popel, P.; Brook-Levinson, F.; Molokanov, V.; Calvo-Dahlborg, M.; Dahlborg, U.; Sidorov, V.; Son, L.; Tarakanov, Y. Influence of the treatment of melt on the properties of amorphous materials: Ribbons, bulks and glass coated microwires. Mater. Sci. Eng. 2001, A304–A306, 54–60. [CrossRef]
27. Popel, P.; Dahlborg, U.; Calvo-Dahlborg, M. On the existence of metastable microheterogeneities in metallic melts. IOP Conf. Ser. Mater. Sci. Eng. 2017, 192, 012012. [CrossRef]
28. Yang, B.; Perepezko, J.H.; Schmelzer, J.W.P.; GaO, Y.; Schick, C. Dependence of crystal nucleation on prior liquid overheating by differential fast scanning calorimeter. J. Chem. Phys. 2014, 140, 104513. [CrossRef]
29. He, Y.; Li, J.; Wang, J.; Kou, H.; Beaunegon, E. Liquid-liquid structure transition and nucleation in undercooled Co-B eutectic alloys. Appl. Phys. A 2017, 123, 391. [CrossRef]
30. Adams, G.; Gibbs, J.H. On the temperature dependence of cooperative relaxation properties in glass-forming liquids. J. Chem. Phys. 1965, 43, 139. [CrossRef]
31. Liu, C.-Y.; He, J.; Keunings, R.; Bailly, C. New linearized relation for the universal viscosity-temperature behavior of polymer melts. Macromolecules 2006, 39, 8867–8869. [CrossRef]
32. Tournier, R.F. Thermodynamic and kinetic origin of the vitreous transition. Intermetallics 2012, 30, 104–110. [CrossRef]
33. Tournier, R.F. Predicting glass-to-glass and liquid-to-liquid phase transitions in supercooled water using classical nucleation theory. Chem. Phys. 2018, 500, 45–53. [CrossRef]
34. Tournier, R.F. Homogeneous nucleation of phase transformations in supercooled water. Phys. B 2020, 579, 411895. [CrossRef]
35. Tournier, R.F. First-order transitions in glasses and melts induced by solid superclusters nucleated by homogeneous nucleation instead of surface melting. Chem. Phys. 2019, 524, 40–54. [CrossRef]
36. Angell, C.A.; Rao, K.J. Configurational excitations in condensed matter and the “bond lattice”. Model for the liquid-glass transition. J. Chem. Phys. 1972, 57, 470–481. [CrossRef]
37. Iwashita, T.; Micholson, D.M.; Egami, T. Elementary excitations and crossover phenomenon in liquids. Phys. Rev. Lett. 2013, 110, 205504. [CrossRef] [PubMed]
38. Ozhovans, M.I. Topological characteristics of bonds in SiO$_2$ and GeO$_2$ oxide systems at glass-liquid transition. J. Exp. Theor. Phys. 2006, 103, 819–829. [CrossRef]
39. Benigni, P. Coupling of phase diagrams and thermochemistry. Calphad 2021, 72, 102228.
40. Wunderlich, B. Study of the change in specific heat of monomeric and polymeric glasses during the glass transition. J. Chem. Phys. 1960, 64, 1052. [CrossRef]
41. Kim, Y.H.; Kiraga, K.; Inoue, A.; Masumoto, T.; Jo, H.H. Crystallization and high mechanical strength of Al-based amorphous alloys. Mater. Trans. 1994, 35, 293–302. [CrossRef]
42. Hu, Q.; Sheng, H.C.; Fu, M.W.; Zeng, X.R. Influence of melt temperature on the Invar effect in (Fe$_{71.2}$B$_{18.4}$Y$_{4.8}$)$_{3}$Nb$_{4}$ bulk metallic glasses. J. Mater. Sci. 2019, 48, 6900–6906.
43. Jiang, H.-R.; Bochtler, B.; Riegler, S.S.; Wei, X.-S.; Neuber, N.; Frey, M.; Gallino, I.; Busch, R.; Shen, J. Thermodynamic and kinetic studies of the Cu-Zr-Al(Sn) bulk metallic glasses. J. Alloys Comp. 2020, 844, 156126. [CrossRef]
44. Yue., Y. Experimental evidence for the existence of an ordered structure in a silicate liquid above its liquidus temperature. J. Non-Cryst. Sol. 2004, 345–346, 523–527. [CrossRef]
45. Wei, S.; Yang, F.; Bednarick, J.; Kaban, I.; Shuleshova, O.; Meyer, A.; Busch, R. Liquid-liquid transition in a strong bulk metallic glass-forming liquid. Nat. Commun. 2013, 4, 2083. [CrossRef] [PubMed]
46. Way, C.; Wadhwa, P.; Busch, R. The influence of shear rate and temperature on the viscosity and fragility of the Zr$_{41.2}$Ti$_{18.5}$Cu$_{25.2}$Ni$_{10.0}$Be$_{8.5}$ metallic-glass-forming liquid. Acta Mater. 2007, 55, 2977–2983. [CrossRef]
47. Lan, L.; Ren, Y.; Wei, X.Y.; Wang, B.; Gilbert, E.P.; Shibayama, T.; Watanabe, S.; Ohnuma, M.; Wang, X.-L. Hidden amorphous phase and reentrant supercooled liquid in Pd-Ni-P metallic glass. Nat. Commun. 2017, 8, 14679. [CrossRef]
48. Tournier, R.F. Glass phase and other multiple liquid-to-liquid transitions resulting from two-liquid competition. *Chem. Phys. Lett.* 2016, 665, 64–70. [CrossRef]

49. Wang, L.-M.; Borick, S.; Angell, C.A. An electrospray technique for hyperquenched glass calorimetry studies: Propylene glycol and di-n-butylphthalate. *J. Non-Cryst. Sol.* 2007, 353, 3829–3837. [CrossRef]

50. Hornboll, L.; Yue, Y. Enthalpy relaxation in hyperquenched glasses of different fragility. *J. Non-Cryst. Sol.* 2008, 354, 1832–1870. [CrossRef]

51. Hu, L.; Zhang, C.; Yue, Y. Thermodynamic anomaly of the sub-$T_g$ relaxation in hyperquenched metallic glasses. *J. Chem. Phys.* 2013, 138, 174508. [CrossRef]

52. Passamani, F.C.; Tagarro, J.R.B.; Lareka, C.; Fernades, A.A.R. Thermal studies and magnetic properties of mechanical alloyed Fe$_2$B. *J. Phys. Cond. Mater.* 2002, 14, 1975–1983. [CrossRef]

53. Tournier, R.F. Crystallization of supercooled liquid elements induced by superclusters containing magic atom numbers. *Metals* 2014, 4, 359–387. [CrossRef]

54. Mpemba, E.B.; Osborne, D.G. Cool? *Phys. Educ.* 1969, 4, 172–175. [CrossRef]

55. Aristotle; Ross, W.D. *Aristotle’s Metaphysics*; Clarendon: Oxford, UK, 1923.

56. Takaiwa, D.; Atano, I.; Koga, K.; Tanaka, H. Phase diagram of water in carbon nanotubes. *PNAS* 2008, 105, 39–43. [CrossRef] [PubMed]

57. Raju, M.; Van Duin, A. Phase transitions of ordered ice in graphene nanocapillaries and carbon nanotubes. *Sci. Rep.* 2018, 8, 3851. [CrossRef] [PubMed]

58. Nie, G.X.; Huang, J.Y.; Huang, J.P. Melting-freezing transition of monolayer water confined by phosphorene plates. *J. Phys. Chem. B* 2016, 120, 9011–9018. [CrossRef]

59. Lu, Z.; Raz, O. Nonequilibrium thermodynamics of the markovian Mpemba effect and its inverse. *PNAS* 2017, 114, 5883–5888. [CrossRef]

60. Kumar, A.; Bechhoefer, J. Exponentially faster cooling in a colloidal system. *Nature* 2020, 584, 64–68. [CrossRef]

61. Kuzmin, V.I.; Tytik, D.L.; Belashchenko, D.K.; Sirenko, A.V. Structure of silver cluster with magic numbers of atoms by data of molecular thermodynamics. *Colloid. J.* 2008, 70, 284–296. [CrossRef]

62. Wu, Q.; Xu, C.; Wu, X.; Cheng, L. Evidence for the super-atom bonding from bond energies. *ACS Omega.* 2018, 3, 14425–14430.

63. Koley, S.; Cui, J.Y.; Panfil, E.; Banin, U. Coupled colloidal quantum dot molecules. *Account Chem. Phys.* 2021, in press. [CrossRef] [PubMed]