Crystal growth nucleation and Fermi energy equalization of intrinsic spherical nuclei in glass-forming melts

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Abstract
The energy saving resulting from the equalization of Fermi energies of a crystal and its melt is added to the Gibbs free-energy change $\Delta G_{2ls}$ associated with a crystal formation in glass-forming melts. This negative contribution being a fraction $\varepsilon_{ls}(T)$ of the fusion heat is created by the electrostatic potential energy $-U_0$ resulting from the electron transfer from the crystal to the melt and is maximum at the melting temperature $T_m$ in agreement with a thermodynamics constraint. The homogeneous nucleation critical temperature $T_2$, the nucleation critical barrier $\Delta G_{2ls}/k_BT$ and the critical radius $R_{2ls}$ are determined as functions of $\varepsilon_{ls}(T)$. In bulk metallic glass forming melts, $\varepsilon_{ls}(T)$ and $T_2$ only depend on the free-volume disappearance temperature $T_{0f}$, and $\varepsilon_{ls}(T_m)$ is larger than 1 ($T_{0f} > T_m/3$); in conventional undercooled melts $\varepsilon_{ls}(T_m)$ is smaller than 1 ($T_{0f} > T_m/3$). Unmelted intrinsic crystals act as growth nuclei reducing $\Delta G_{2ls}/k_BT$ and the nucleation time. The temperature-time transformation diagrams of Mg$_{65}$Y$_{10}$Cu$_{25}$, Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$, Pd$_{43}$Cu$_{27}$Ni$_{10}$P$_{20}$, Fe$_{83}$B$_{17}$ and Ni melts are predicted using classic nucleation models including time lags in transient nucleation, by varying the intrinsic nucleus contribution to the reduction of $\Delta G_{2ls}/k_BT$. The energy-saving coefficient $\varepsilon_{nm}(T)$ of an unmelted crystal of radius $R_{nm}$ is reduced when $R_{nm} \ll R_{2ls}$; $\varepsilon_{nm}$ is quantified and corresponds to the first energy level of one s-electron moving in vacuum in the same spherical attractive potential $-U_0$ despite the fact that the charge screening is built by many-body effects.

Keywords: metallic glasses, intrinsic growth nuclei, crystal nucleation, Fermi energy effects, unmelted intrinsic crystals, glass-forming melts

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Transformations such as liquid–solid or solid–liquid always induce changes in the conduction electron number per unit volume and sometimes per atom. The equalization of Fermi energies of a tiny particle having a radius smaller than a critical value and its melt produces an unknown energy saving $-\varepsilon_v$ equal to a fraction $\varepsilon_{ls}$ of the fusion heat per unit volume. All crystal nucleation models describe the crystallization without taking account of $\varepsilon_v$ in metallic alloys [1–3]; they have predicted that unmelted crystals are absent above the melting temperature $T_m$ and that the solidification is governed by a homogeneous nucleation if extrinsic nuclei are absent. The unknown contribution $-\varepsilon_v$ has recently been added to the Gibbs free-energy change $\Delta G_{2ls}(\theta)$ associated with a nucleus formation in 38 liquid elements; the new critical energy barrier and the new surface energy are compatible with $\varepsilon_{ls0} = \varepsilon_{ls}(\theta = 0) = 0.217$, where $\theta = T/T_m - 1$; in this model, tiny
intrinsic crystals can survive above the melting temperature and act as heterogeneous nuclei for crystallization of a melt above a unique homogeneous nucleation critical temperature $T_0 = \frac{T_m}{3}$ or $\theta_0 = -2/3$. The thermal variation of $\varepsilon_{ls}$ is an even function of $\theta$ having a maximum value $\varepsilon_{ls0}$ for $T = T_m$: $\varepsilon_{ls}$ is equal to zero for $\theta = -2/3$ or $T = T_m/3$ in agreement with the disappearance temperature $T_{0l} = T_m/3$ or $\theta_{0l} = -2/3$ of the free volume in liquid elements [4–6].

The same analysis is applied to metallic glass-forming melts because large values of $\varepsilon_{ls0}$ induced by large relative changes $\Delta E_F/E_F$ of the Fermi energy $E_F$ are expected for two reasons: (i) a solidified eutectic alloy is composed of solid particles having compositions, densities and Fermi energies different from that of the melt [7] and (ii) conduction-electron weak-localization effects are stronger in undercooled melts than in crystallized alloys [8–10].

The $\theta^2$ dependence of the electronic energy saving coefficients $\varepsilon_{ls}(\theta)$ of crystals reaching the critical size is determined on the basis of a thermodynamic constraint at the melting temperature. The glass-forming ability of any metallic melt is determined on the basis of a thermodynamic constraint at the melting temperature.

The unmelted crystal contribution $\Delta G_{mn}$ to the free-energy change associated with crystal formation is dependent on its radius $R_{mn}$ and on its own energy saving coefficient $\varepsilon_{nm0}$: $\Delta G_{mn}$ reduces the critical energy barrier and is used as an adjustable parameter to calculate a temperature-time transformation (TTT) diagram in agreement with the experimental results in $\text{Mg}_{82}\text{Y}_{10}\text{Cu}_{18}$, $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$, $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{9}\text{P}_{20}$ and $\text{Fe}_{83}\text{B}_{17}$ taking account of time lags in transient nucleation [11–18]. Direct observations of mean range order (MRO) regions in a conventional glass $\text{Fe}_{83}\text{B}_{17}$ are also used to test the model validity by assuming that these regions correspond to unmelted crystals. At low radius $R_{mn} \ll R_{2ls}$, $\varepsilon_{nm0}$ is much smaller than $\varepsilon_{ls0}$.

The free-electron transfer $e \cdot n \cdot \Delta \varepsilon$ creates a crystal charge screened by conduction electrons moving around spherical crystals and by an electrostatic potential energy $-U_0$, $n$ being the number of atoms in the crystal and $\Delta \varepsilon$ the charge number excess per atom. Quantum effects are expected to reduce the electronic energy saving as compared with the potential energy. The first quantified energy level of a conduction electron moving in vacuum in the same spherical attractive potential well $-U_0$ is compared with the experimental energy saving $\varepsilon_{ls}$ obtained in a metallic melt despite the fact that, in a metal, the charge screening is built by many-body effects.

Metallic glasses are quenched with cooling rates $R_c$ varying from $10^6$ to 0.004 K s$^{-1}$ and depending on the elements involved in their composition [7, 10–12, 19]. Above the glass temperature $T_g$, the first crystallization at a temperature $T_k$ is produced in the undercooled liquid region using a heating rate $R_h$ (K s$^{-1}$) from the glass state; the transformation curves $T (t)$ have a nearly parabolic behavior with a nose temperature $T_{n0}(\theta_0)$. The critical cooling rate $R_{c0}$ (K s$^{-1}$) $= \frac{T_{0l}-T_m}{k_BT_m}$ applied to the melt without crystallization and the heating rate $R_h$ (K s$^{-1}$) strongly depend on the presence of heterogeneous nuclei as recently confirmed for some Pd–Ni–Cu–P alloys; $R_c$ can be decreased by three orders of magnitude [17, 20] during temperature cycling of samples from the glass state to a liquid state far above $T_m$.

2. Main results of a revisited crystal nucleation model

The classic growth nucleation model, in its present state, cannot be used to calculate the TTT curves because it predicts a large increase and a divergence of the energy barrier when $T$ approaches the melting temperature [1, 2, 11, 12, 21]. The new analysis of liquid undercooling experiments leads to the following formulae (1–6) [4–6]: the Gibbs free-energy change for a crystal formation given by (1) takes account of the energy saving $\varepsilon_c$ related to the equalization of the particle Fermi energy to that of the melt

$$\Delta G_{2ls}(\theta) = (\Delta G_c - \varepsilon_c)\frac{R^3}{3} + 4\pi R^2 \varepsilon_{2ls}. \quad (1)$$

Here $R$ is the crystal radius; the surface energy $\sigma_{2ls}$ [1], $\Delta G_c$ and $\varepsilon_c$ are as expressed as follows

$$\sigma_{2ls} = \sigma_{2ls0} \left( \frac{\Delta H_m}{V_m} \right)^{1/3}, \quad \Delta G_c = \frac{\Delta H_m}{V_m} \theta, \quad \varepsilon_c = \frac{\Delta H_m}{V_m}.$$

Here $\Delta G_{2ls}$ is the fusion enthalpy per molar, $V_m$ is the molar volume, $\sigma_{2ls0}$ is defined by (6). In $[K_i(\theta)] \leq 90 \pm 2$ or $[K_i] \leq 10^{90 \pm 1}$ m$^{-3}$ s$^{-1}$; $\theta = \frac{T_m-T}{T_m}$ corresponds to the free-volume disappearance temperature $T_{0l}$; the fraction $\varepsilon_{ls}$ of the fusion heat per unit volume is an even function of $\theta$ as observed in many liquid elements and shown in figure 1. It has a maximum $\varepsilon_{ls0}$ at the melting temperature ($\theta = 0$) is equal to zero for $\theta = \theta_{0l}$ or $T = T_{0l}$ regardless of the $\varepsilon_{ls0}$ amplitude [4–6]. The electronic energy coefficient $\varepsilon_{ls0}(\theta)$ being related to the free-electron density difference is expected to disappear with the free volume, $\varepsilon_{ls0} = 0$ when $\Delta V_m/V_m = 0$ for $\theta = \theta_{0l}$ and is maximum for $\varepsilon_{ls0} = \varepsilon_{ls0}$ when $\Delta V_m/V_m$ is maximum for $\theta = 0$; the derivative $\frac{3d(\Delta G_{2ls})}{4\pi R^2 dR}$ has to be positive and equal to the fusion entropy per unit volume $\frac{\Delta S}{T}$ at the equilibrium temperature $\theta = 0$ ($T = T_m$) of a bulk sample; this condition is met by (2) because $\left( \frac{d(\Delta G_{2ls})}{R^2 dR} \right)_{T=T_m} = 0$. The contribution $O(\theta^4)$ to (2) is neglected.

As already shown [4–6], the new critical radius $R_{2ls}^c(\theta)$ and the new critical energy barrier $\frac{\Delta G_{2ls}^c}{k_BT}$ given by (3) are calculated setting $d(\Delta G_{2ls})/dR = 0$ and assuming that the surface energy becomes independent of the radius for $R \gg R_{2ls}^c(\theta)$, with $\frac{d\sigma_{2ls}}{dR} = 0$ or $\left( \frac{d\frac{\Delta G_{2ls}}{R^2}}{dR} \right)_{R < R_{2ls}}$ being negligible:

$$\frac{\Delta G_{2ls}^c}{k_BT} = \frac{16\pi \Delta S_m \varepsilon_{2ls}}{3N_k(\theta-\varepsilon_{ls})^2(1+\theta)}, \quad R_{2ls}^c = -2\frac{\sigma_{2ls}}{\theta-\varepsilon_{ls}} \left( \frac{V_m}{N_k} \right)^{1/3}. \quad (3)$$
The free-volume disappearance temperature \( T_{0l} \) is chosen in (8) to be equal to the VFT temperature \( T_{\text{VFT}} \) of Mg_{63}Y_{10}Cu_{25}, Zr_{41.2}Ti_{13.8}Cu_{25}Ni_{10}Be_{22.5}, Pd_{33}Cu_{27}Ni_{10}P_{20} \) and equal to \( T_{0l}/3 \) in Fe_{83}B_{17}. Note that combining the VFT equation (8) with the Doohittle relation defining the viscosity as a function of the free volume leads to \( T_{0l} = T_{\text{VFT}} [11, 23, 24] \). This equality is proved with a free-volume measurement of a Pd_{33}Cu_{27}Ni_{10}P_{20} melt and a viscosity measurement of a Pd_{90}Ni_{10}Cu_{10}P_{30} melt; the VFT temperature is equal to 447 K [14, 15]; a linear extrapolation of the Pd_{33}Cu_{27}Ni_{10}P_{20} glass volume to the critical volume leads to \( T_{0l} = 452.3 \) K [25].

All the free volumes would tend to be zero at \( T = T_{0l} \) or \( \theta = \theta_0 \) in the absence of a glass transition; the temperature \( T_{0l} \)
of the undercooled melt is extrapolated below $T_g$ by using (8) for the thermal variation of the melt viscosity [11, 22, 23]; $D^*$ is the glass-fragility parameter; $\ln(K_{ls})$ is chosen equal to

$$
\ln(K_{ls}) = \ln\left(\frac{\eta A}{\eta_l}\right) = (\ln A) \pm 2 - \frac{D^* T_{0l}}{(T - T_{0l})}. 
$$

The numerical constant $\ln A \leq 90$ or $A \leq 10^{39.1} \text{m}^{-3} \text{s}^{-1}$ in (9) can be slightly changed for alloys [21]; the viscosity of pure liquid elements is of the order of 0.002 Pa s and of $\eta_0$; $\ln(K_{ls})$ is not strongly varying among many liquid elements and is equal to $\ln A = 90 \pm 2$ [3, 4]. The values of $T_m$, $\Delta H_m$, $V_m$, $T_g$, $\theta_2$, $T_{0l}$, $\theta_0$, $D^*$, $\theta_2$, and $\varepsilon_{ls0}$ of some undercooled melts are given in table 1.

3. Metallic glass-forming melts classified on the basis of an electronic energy saving coefficient $\varepsilon_{ls0}$ smaller or larger than 1

It is possible to calculate $\varepsilon_{ls0}$ of each alloy only knowing $T_{0l}$ or $\theta_0$. Equation (10) is obtained applying (2) and (5) for $\theta = \theta_2$

$$
\frac{\theta_2^2 \varepsilon_{ls0}}{\theta_{0l}^2} + 3 \theta_2 + 2 - \varepsilon_{ls0} = 0.
$$

There are two solutions for $\theta_2$ when $\varepsilon_{ls0}$ is larger than a minimum value corresponding to the minimum electronic energy saving as described in figure 2; the relations (11) between $\varepsilon_{ls0}$, $\theta_2$, and $\theta_{0l}$ are met when $\varepsilon_{ls0}$ is minimum and larger than 1

$$
\theta_{0l}^2 = \frac{1}{4}(4 \theta_2 + 3 \theta_2^2), \quad \varepsilon_{ls0} = \frac{1}{2} \theta_2^2, \quad \theta_{ls0} = 1.5 \times \theta_2 + 2.
$$

The second relation in (11) is obtained by equalizing the derivatives of (2) and (5). The knowledge of $\theta_0$ and the use of (11) determine $\varepsilon_{ls0}$ and $\theta_2$ of any alloy having $\varepsilon_{ls0} > 1$ as given in table 1 for several glass-forming melts; $\theta_2$ is always larger than $-2/3$ for $\varepsilon_{ls0} > 1$ or for $\theta_0 > -2/3$ as shown in figure 2; $\theta_2 = \theta_0 = -2/3$ for $\varepsilon_{ls0} \leq 1$.

The existence of two glass-former classes is then predicted. The bulk metallic glasses correspond to $\varepsilon_{ls0} > 1$ and $\theta_0 > -2/3$, while and conventional glasses to $\varepsilon_{ls0} < 1$ and $\theta_0 = -2/3$. The glass-forming ability of bulk metallic glass-forming melts satisfying $T_{0l} > T_m/3$ can be defined using values of $\varepsilon_{ls0}$ larger than one, $\varepsilon_{ls0}$ being calculated using (11) from the knowledge of the free-volume disappearance temperature $T_{0l}$. The isothermal structural relaxation tends to reduce the free-volume excess frozen by rapid cooling [7]; out-of-equilibrium values of $\varepsilon_{ls0}$ are then obtained by quenching and are relaxing down to a minimum value given by (11). There is no minimum value of $\varepsilon_{ls0}$ below 1 except $\varepsilon_{ls0} = 0$.

The free-volume disappearance temperature $T_{0l}$ is observable in spite of its freezing at $T = T_g$ because a PD$_3$Cu$_{27}$Ni$_{10}$P$_{20}$ specific-heat slope change in the glass state can be observed at this temperature $T_g$ (see figure 2 of [13]) when the glass specific heat becomes equal to the crystal one; this temperature is also deduced as being equal to $T_{VFT}$ from measurements of the equilibrium viscosity of the undercooled melt using (8).

---

Table 1. The melting temperature $T_m$, fusion heat $\Delta H_m$ per mole, molar volume $V_m$, glass transition temperatures $T_g$ and $\theta_g = (T_g - T_m)/T_m$, Vogel–Fulcher-Tammann temperature $T_{0l}$ of the undercooled melt, $\theta_0 = (T_0 - T_m)/T_m$, glass fragility $D^*$ $\ln A$ as defined by (9), electronic energy saving coefficient $\varepsilon_{ls0}$ at $T = T_m$ associated with a crystal formation and $\theta_2$ are given for various melts with some references; the alloys no. 1 and no. 2 are Zr$_{41.2}$Ti$_{13.8}$Cu$_{15.8}$Ni$_{10}$Be$_{22.8}$ and Pd$_{41}$Ni$_{10}$Cu$_{22}$P$_{20}$, respectively.

| Alloy          | $T_m$(K) | $\Delta H_m$(J) | $V_m$(cm$^3$) | $T_g$(K) | $\theta_g$ | $T_{0l}$(K) | $\theta_0$ | $D^*$ | $\varepsilon_{ls0}$ | $\theta_2$ |
|---------------|----------|-----------------|---------------|----------|------------|-------------|------------|------|---------------------|-----------|
| 1-PdCuNiP     | 802      | 7010            | 8             | 585      | -0.271     | 452.3       | -0.436     | 9.14 | 1.76                | -0.162    |
| 2-ZrTiCuNiBe  | 937      | 6184            | 625           | 420      | -0.333     | 412.5       | -0.56      | 1.54 | 1.23                | 0.510     |
| 3-Mg$_6$Y$_{10}$Cu$_{25}$ | 739 | 8650           | 13.3          | 260      | -0.432     | 22.1        | 10.4       | 1.23 | -0.217              | 0.3       |
| 4-Nickel      | 1725     | 17500           | 7.43          | 575      | -0.754     | 575         | 0          | 1.23 | 0.666               | 0.666     |
| 5-PdFeB       | 1447     | 13250           | 6.55          | 482      | -0.534     | 3.0         | 10        | 0.666              | 0.666     |

References [13, 25–29] [18, 26] [27] [4, 19] [34, 35]
4. Temperature-time-transformation diagrams

The calculation of the first-crystallization nucleation time \( t \) has to take into account not only the steady-state nucleation time \( t_{ns} \) but also the time lag \( t_{ns} \) in transient nucleation [11] with

\[
t = t_{ns} + \frac{\pi^2}{6} t_{ns}, \quad \text{when} \quad t \gg \frac{\pi^2}{6} t_{ns},
\]

\[
J = \frac{a_0^2 N}{2\pi \Gamma} \exp \left( -\frac{\Delta G_{eff}}{k_B T} \right),
\]

where \( \Gamma = \left( \frac{1}{3\pi k_B T} \right)^{1/2} \), \( \tau_{ns} = \frac{a_0^2 N}{2\pi \Gamma} \).

The time lag \( t_{ns} \) is proportional to the viscosity \( \eta \) while the steady-state nucleation rate \( J \) is proportional to \( \eta^{-1} \); the coefficient of \( J \) in (13) is not dependent on \( \eta \) [11, p 270]; \( \Gamma \) is the Zeldovich factor, \( a_0^2 = \pi^2/6 \), \( N \) the number of atoms per unit volume, \( \eta \) the number of atoms in the critical sphere; \( K_{ls} \) is defined by (9); equation (12) will also be applied when \( t_{ns} \) is small compared with the time lag \( \tau_{ns} \); a very small value of \( \tau_{ns} \) undervalues the time \( t \) by a factor 2 or 3 and has a negligible effect in a logarithmic scale [11]. The first crystallization occurs when \( J = (vt_{ns})^{-1} \) in the presence of an intrinsic growth nuclei, \( v \) being the sample volume. The critical energy barrier is obtained using (3) and the values of \( \varepsilon_n \) as a function of \( \theta^2 \); \( t_{ns} \) is deduced from (7) with \( \ln(K_{ls}) \) given by (9). The various parameters used in these calculations are given in table 1. The energy barrier \( \Delta G_{nm} \) of intrinsic nuclei is calculated using (1); the radius \( R_{nm} \) is temperature-independent down to the growth temperature; \( \varepsilon_{nm}(\theta) \) is assumed to vary as \( \varepsilon_{ls}(\theta) \) given by (2).

The crystal of radius \( R_{nm} \) can act as a growth nucleus at any temperature \( T \leq T_mB \) when \( \Delta G_{nm}/k_B T \) is equal to \( \ln(K_{ls}(\theta)\psi) \). The intrinsic unmelted crystals also induce the crystallization at the melting temperature \( T_mB \) when the melt has been weakly overheated [4]. The free-energy change definition could be criticized when the cluster is so small that it mainly contains surface atoms [2]. In this case, the calculation of the TTT diagrams will show that the energy-saving coefficient \( \varepsilon_{nm}(\theta = 0) \) of very small unmelted crystals is strongly weakened compared with \( \varepsilon_{ls} \) for \( n = 8 \sim 9 \) atoms; this reduction shows that \( \varepsilon_{nm}(\theta = 0) \) depends on the radius \( R_{nm} \); the use of \( \varepsilon_{ls} \) to calculate \( R_{nm} \) in Fe83B17 and in pure liquid elements when \( R_{nm} \) is a large fraction of the critical radius [4–6] is nevertheless successful.

The time lag is easily obtained when \( t_{ns} \) has been determined. The effect of \( t_{ns} \) in (12) is very important below the nose temperature of the TTT diagram and near the glass transition. It tends to stabilize the nose temperature somewhere between \( T_mB \) and \( T_g \) and to protect the undercooled melt from crystallization; it determines a large fraction of the first-crystallization nucleation time between the nose temperature and the glass transition. The steady-state

nucleation time \( t_{ns} \) is minimum at temperatures much lower than the nose temperature \( T_mB \); then, \( T_mB \) results from the competition between the increase in the time lag \( t_{ns} \) and the decrease in \( t_{ns} \) with decreasing temperature.

4.1. Zr41.2Ti13.8Cu12.5Ni10Be22.5

The TTT diagram has been studied using a containerless electrostatic levitation technique [18]. The nose temperature and nose time are 800 K and 70 s, respectively. The TTT curves represented in figure 3 are calculated using the parameters given in table 1 with a sample volume \( v = 2.5 \text{ mm}^3 \) [18, 26]. The value of \( \ln A \) determines the nose temperature; the nose temperature no. 1 calculated with \( \ln A = 90 \) is much smaller than the others calculated with \( \ln A = 86 \). The TTT diagram no. 3 calculated with \( \ln A = 86 \), \( \varepsilon_{ls} = 1.54 \), \( \varepsilon_{nm} = 1.54 \) and \( R_{nm} = 0.404 \text{ nm} \) is too wide compared with the experimental ones (figure 4 in [18]). The black triangles (dataset 5) are experimental points from [18].

The values of \( \Delta G_{nm}/k_B T \) corresponding to the TTT curves in figure 3 are represented in figure 4 by a diagram \( \Delta G_{nm}/k_B T \) (T). The TTT diagram width becomes narrower using series 4 calculated points with \( \varepsilon_{nm} = 0.91 \) and in good agreement with the experimental results of [18]; it is only modified by the variation of \( \Delta G_{nm}/k_B T \), \( R_{nm} \) and \( \varepsilon_{nm} \) being hidden variables.

These unmelted solid particles would have to melt when \( \varepsilon_{ls}(\theta) = 0.91 \times (1 - 3.189 \theta^2) \); this disappearance is
expected for $\theta = 0.41$ or $T = 1.41 \times T_m$ or $1.41 \times T_i$. $T_m = 937$ K and $T_i = 993$ K being the liquidus temperature. This event would occur in the range of 1321–1400 K. An abrupt increase in the crystallization time has been observed at 830 K after an overheating in the range of 1250–1300 K [18]; all unmelted clusters do not disappear above this temperature range because near-eutectic compositions contain several unmelted clusters do not disappear above this temperature range because near-eutectic compositions contain several compounds that have melting temperatures higher than $T_m$; the model developed here uses a mean composition and a unique melting temperature.

4.2. Mg$_{65}$Y$_{10}$Cu$_{25}$

The glass transition $T_g$ and the crystallization temperature of Mg$_{65}$Y$_{10}$Cu$_{25}$ alloy were measured in differential scanning calorimetry (DSC) scans with various heating rates $R_h$ (K s$^{-1}$) and cooling rates $R_c$ (K s$^{-1}$); $T_g$ is slightly increased from 400 to 420 K with $R_h$ (K s$^{-1}$) varying from 0.002 to 10 K s$^{-1}$ [27] while the glass-undercooled melt transformation extends from 420 to 453 K. The alloy melting occurs between 730 and 739 K. The sample weights vary from 4 to 50 mg. Calculations using the parameters indicated in table 1 and $\ln A = 90$ in two experiments. The TTT diagrams are indicated in figure 5 by $T[R_c$(K s$^{-1}$)]) above the nose temperature $T_n$ and $T[R_h$(K s$^{-1}$)]) below $T_n$. $R_h$ and $R_c$ being the cooling and heating rates, respectively, given by $(T - T_n)/t$ and $(T - T_g)/t$ and $t$ being the nucleation calculated time at the temperature $T$. The curve 1 is calculated with $\ln A = 90$, $\varepsilon_{\text{eff}} = 1.23$, $R_{\text{am}} = 0.225$ nm, $v = 16.4$ nm$^3$; its width is still very broad and the crystal would only contain 3 atoms. In contrast, the curve 2 is obtained with $\varepsilon_{\text{eff}} = 1.23$, $\varepsilon_{\text{am}} = 1.03$, $R_{\text{am}} = 0.36$ nm, $v = 2.7$ nm$^3$; the only change in the series 3 curve is the sample volume $v$ equal to 16.4 nm$^3$; the increase in $v$ moves the nose to a higher critical cooling rate $R_{cc}$ without changing its width.

Several experimental points extracted from [27] represented in figure 5 by series 5 are in good agreement with the series 3 curve; $T_n = 590$ K and $t_n = 10450$ K s$^{-1}$ are obtained. A particle having a radius $R_{\text{am}} = 0.36$ nm contains 8.8 atoms on average. The nose is more pointed than expected in [27]; the nose time and cooling rate are modified using the same factor when the volume is changed. Here, too, the TTT curves below the nose temperature do not depend on the contribution of heterogeneous intrinsic nuclei to the critical barrier because the time lag $t_{\text{am}}$ becomes much larger than the steady-state nucleation time $t_n$. The calculated TTT diagrams can be compared with the experimental ones represented in figure 6 of [27].

4.3. Pd$_{43}$Ni$_{110}$Cu$_{27}$P$_{20}$

The DSC thermograms of this glass have been studied by isothermal crystallization at various temperatures using a few milligrams of samples processed in B$_2$O$_3$ [16, 17, 28–31]. The first growth event corresponding to 1% crystallization is not reproducible above 700 K; a large dispersion of times has been observed as shown in refs. [14, 15, 17, 20] and indicated in figure 7 by horizontal bars. The points measured below 700 K are much less dispersed and used to evaluate $\ln A$ and the contribution $\Delta G_{\text{am}}/k_B T$ of heterogeneous intrinsic nuclei to the reduction of the critical energy barrier given by (7). Four TTT diagrams are plotted with the same sample volume $v = 0.32$ mm$^3$ chosen by experimentalists [18] and calculated with parameters given in table 1; the first curve on the left corresponds to $\ln A = 90$, $\varepsilon_{\text{am}} = 1.23$, $R_{\text{am}} = 0.194$ nm and a nose temperature of 714 K. The only change in the second one is $\ln A = 84$. These two TTT diagrams have a very broad temperature width compared with the experimental results indicated by horizontal bars. The dispersion above 700 K is due to changes in the heterogeneous nuclei contribution depending on the temperature cycling of samples [20]. Various values of $t$ are obtained each time that
The nucleation rate $J$ in pure liquid elements has a maximum as a function of $\ln T$ because $0$. The critical radius becomes constant for $v$ of parameters given in table 1. The TTT diagrams calculated with $R_{\text{nm}}/R_{2ls}(\theta = 0)$ would occur below $T_2 = T_{\text{m}}/3$ at $T_k = T_g$. The product of the sample volume and nucleation time of a nickel melt is plotted versus $\theta = (T - T_{\text{m}})/T_{\text{m}}$. In $A = 90$ has been previously determined [3, 4]. The sample volumes are $1.0 \times 10^{-11}$ and $1.0 \times 10^{-10}$ m$^3$ from bottom to top. The calculation parameters are given in table 1. The kink at $\theta_k = -2/3$ corresponds to $\epsilon_{\text{m}} = 0$ [4]. The first crystallization temperature $T_0$ would occur below $T_2 = T_{\text{m}}/3$ at $T_k = T_g$.

4.5. Calculated TTT diagram of Fe$_3$B$_{17}$ and the direct observations of ‘medium range order’ regions in as-quenched amorphous ribbons

The density of nuclei in the glass state is typically of the order $10^{23}$ to $10^{24}$ m$^{-3}$ far above the density of homogeneous nuclei calculated using the classic nucleation model [33]. The magnetic field texturing obtained after application of a very low cooling rate still produces about $10^{21}$–$10^{22}$ crystals per m$^3$ as deduced from crystal radii equal to about 50 nm [4, 5]. Evaluations of their initial size in metallic glasses have been made after quenching Fe$_3$B$_{14}$, Fe$_3$B$_{17}$ and Fe$_8$B$_{20}$ ribbons and by studying their microstructure by high-resolution transmission electron microscopy (HRTEM) and other techniques. Local cluster structures of bcc-Fe and Fe boride having diameters of 1.5–2 and 1 nm diameter are directly observed and are a strong indication of a “nanoscale phase separation” in the amorphous phase [33]. These regions are observed at room temperature with a very diffuse interface. They could have a sharper interface in the undercooled melt above the glass transition. It is suggested that these clusters could be the unmelted crystals surviving above the melting temperature.

Fe$_3$B$_{17}$ is a eutectic having a melting temperature of 1447 K leading to a conventional glass obtained by melt spinning. Ribbons could have a thickness of 30 μm. The disappearance of the glass state depends on the heating rate $R_h$ and is accompanied by crystallization. $T_g = T_k = 625$ K when $R_h = 0.016$ K s$^{-1}$ and $T_g = T_k = 675$ K when $R_h = 0.33$ K s$^{-1}$ [34]. The TTT diagram can be calculated with a new sample is studied at the same temperature [17]. This phenomenon has been viewed as being due to impurity nuclei governing the nucleation above 700 K; in particular, the $T (t)$ noses are translated along the $t$ axis when fluxed and unfluxed materials are compared [32]. This could be due to the fact that the contribution of intrinsic nuclei to the reduction of the critical energy barrier above $T_k$ would be smaller than the impurity one.

The first TTT narrow curve on the left of figure 6 having $T_0 = 680$ K and $t_0 = 125$ s has been calculated with a radius $R_{\text{nm}} = 0.295$ nm, $A = 84$ and $\epsilon_{\text{nm}} = 0.93$; the last one on the right having $T_0 = 660$ K, $t_0 = 764$ s, $A = 84$, $R_{\text{nm}} = 0.29$ nm, and $\epsilon_{\text{nm}} = 0.89$ corresponds to longer times experimentally observed above $T_k$ [17] as well as in Pd$_{43}$Cu$_{27}$Ni$_{10}$P$_{20}$ and Pd$_{43}$Cu$_{27}$Ni$_{10}$P$_{20}$ [20, 30, 31]. An unmelted crystal would contain about 7.9 atoms on average for $R_{\text{nm}} = 0.295$ nm. There is some uncertainty on $\epsilon_{\text{nm}}$ because $0.89 < \epsilon_{\text{nm}} < 0.93$ is determined on the basis of an experimental width of the TTT curve that is not reproducible as a function of $\ln t$.

4.4. Nickel

The nucleation rate $J$ in pure liquid elements has a maximum value for $\theta = 0 = -2/3$ [4]. The time lag is negligible. The glass transition would occur at $T = 0.246T_{\text{m}}$ as indicated in [19]; the heating rate used to determine the glass transition would be 12 orders of magnitude smaller than the critical cooling rate [19]. The TTT diagrams calculated with parameters given in table 1 are represented as a function of $v = \ln t$ in figure 7 for different values of $R_{\text{nm}}/R_{2ls}(\theta = 0)$; $v$ being the sample volume. The energy-saving coefficient is equal to zero and the critical radius becomes constant for $\theta < -0.666$. There is a good agreement with expectations [19]; the glass state could be obtained using $R_{\text{cm}} = 3 \times 10^{10}$ K s$^{-1}$ corresponding to a nose time equal to 38 ns. The unmelted crystal would have to contain 59 or 102 nickel atoms; such small number of atoms could be obtained by overheating the melt above 2072 K [4]; the sample volume would have to be of the order of 2.6 mm$^3$ when $R_{\text{nm}}/R_{2ls}(\theta = 0) = 0.11$ and to be much smaller for larger values of $R_{\text{nm}}/R_{2ls}(\theta = 0)$.

![Figure 6](image-url) The first crystallization temperature of Pd$_{43}$Cu$_{27}$Ni$_{10}$P$_{20}$ plotted versus the crystallization time logarithm; calculations were performed with $v = 0.32$ mm$^3$ and the parameters given in table 1 [13, 28, 29]: Curve 1 $A = 90$, $\epsilon_{\text{nm}} = 1.76$, $\epsilon_{\text{m}} = 1.76$, $T_a = 714$ K, $R_{\text{nm}} = 0.194$ nm; Curve 2 ($\times$) $A = 84$, $\epsilon_{\text{nm}} = 1.76$, $T_a = 714$ K, $R_{\text{nm}} = 0.194$ nm; Curve 3 $A = 84$, $\epsilon_{\text{nm}} = 1.76$, $T_a = 0.93$, $T_k = 680$ K, $t_0 = 125$ s, $R_{\text{nm}} = 0.295$ nm; Curve 4 $A = 84$, $\epsilon_{\text{nm}} = 1.76$, $R_{\text{nm}} = 0.89$, $T_k = 660$ K, $t_0 = 764$ s, $R_{\text{nm}} = 0.29$ nm. The double arrows correspond to the experimental spread [17, 20].

![Figure 7](image-url) The product of the sample volume and nucleation time of a nickel melt is plotted versus $\theta = (T - T_{\text{m}})/T_{\text{m}}$. In $A = 90$ has been previously determined [3, 4]. The sample volumes are $1.0 \times 10^{-11}$ and $1.0 \times 10^{-10}$ m$^3$ from bottom to top. The calculation parameters are given in table 1. The kink at $\theta_k = -2/3$ corresponds to $\epsilon_{\text{m}} = 0$ [4]. The first crystallization temperature $T_0$ would occur below $T_2 = T_{\text{m}}/3$ at $T_k = T_g$. There is some uncertainty on $\epsilon_{\text{nm}}$ because $0.89 < \epsilon_{\text{nm}} < 0.93$ is determined on the basis of an experimental width of the TTT curve that is not reproducible as a function of $\ln t$. The density of nuclei in the glass state is typically of the order $10^{23}$ to $10^{24}$ m$^{-3}$ far above the density of homogeneous nuclei calculated using the classic nucleation model [33]. The magnetic field texturing obtained after application of a very low cooling rate still produces about $10^{21}$–$10^{22}$ crystals per m$^3$ as deduced from crystal radii equal to about 50 nm [4, 5]. Evaluations of their initial size in metallic glasses have been made after quenching Fe$_3$B$_{14}$, Fe$_3$B$_{17}$ and Fe$_8$B$_{20}$ ribbons and by studying their microstructure by high-resolution transmission electron microscopy (HRTEM) and other techniques. Local cluster structures of bcc-Fe and Fe boride having diameters of 1.5–2 and 1 nm diameter are directly observed and are a strong indication of a “nanoscale phase separation” in the amorphous phase [33]. These regions are observed at room temperature with a very diffuse interface. They could have a sharper interface in the undercooled melt above the glass transition. It is suggested that these clusters could be the unmelted crystals surviving above the melting temperature.
In a metal, the charge is screened around the crystal surface by the introduction in the medium of an equivalent number of electron charges, but their distribution is not uniform in a large volume of the metal and may be better represented by a point charge. This charge is called the macroscopic electron charge and is equal to the chemical equivalent of the metal, multiplied by the number of moles of the element in the medium. The electrostatic potential energy of the crystal nucleus and its melt can be calculated using

$$\Delta E_F = \frac{h^2 (3\pi^2)^{2/3}}{3m} \left( \frac{N_A}{V_m} \right)^{2/3} v^{-1/3}$$

(14)

Equation (14) is applied to the following liquid elements: Ti, Fe, Co, Ni, Zn, Pd, Cd, Pt, Au, Al, In, Sn and Pb assuming $\Delta v = 0$; $V_m/V_m$ is extrapolated up to the melting temperature from the thermal variation of the expansion coefficient and given in table 2 [4, 36, 37].

$$\frac{\Delta E_F}{E_F} = \frac{2 \Delta V_m}{3 V_m}$$

(15)

$\Delta E_F$ can be calculated if $v$ is known: the ultrasound velocity $a_0$ in liquid elements at $T = T_m$ is related to $v E_F$ as shown by (16), $M$ being the atomic mass [4, 38].

The electrostatic potential energy $-U_0$ induced by a crystal of large radius $R = R_{m0}$ containing $n$ atoms at the melting temperature would have to be nearly equal to $E_F$, the quantified energy given by (17), because it carries a large charge $n \Delta z_F \cdot e$; an analogy is made with clusters carrying electric charges in an inert medium [40–42] with electron correlations being neglected.

$$U_0 = \frac{n \Delta z_F e^2}{8\pi \varepsilon_0 R} \approx E_F = \frac{n\varepsilon_0 \Delta H_m}{N_A}$$

(17)

In a metal, the charge is screened around the crystal surface by the free electrons of the melt; equation (17) contains the vacuum permittivity $\varepsilon_0 = 8.85 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$ and the electron charge $e = 1.602 \times 10^{-19} \text{ C}$; it is applied to the 13 liquid elements for $T = T_m$ using $R = R_{m0}(R_0 = 0)$ given in table 2 and $\varepsilon_0 = 0.217$ in order to determine $\Delta z_F$. The quantities $\Delta z_F$ determined from (14–16) and $\Delta z_F$ deduced

5. Fermi energy equalization of a spherical crystal and its melt induced by electron transfer

5.1. Formulation of the electrostatic potential induced by a charged crystal

The electrostatic energy saving $\varepsilon_s$ is associated with the Fermi-energy equalization of crystal nuclei and their melt.
Table 2. The following quantities characterizing 13 elements are given at $T = T_m$ from left to right: (1) $R^*_{2n} \times 10^{-28}$ is the critical radius for crystal growth; (2) $N_{\Delta z} / V_{m}$ is the atomic number per m$^3$; (3) $M_{\Delta z}^2$ is the atomic mass multiplied by the ultrasound velocity in the liquid state; (4) $v$ is the number of conduction electrons per atom deduced from (14–16); (5) $\Delta U_{V_m}$ is the relative free volume; (6) $\Delta H_{m}$ is the fusion heat per mole; (7) $\Delta z_{F}$ is the free-electron number difference per atom calculated with (14–16); (8) $\Delta q_{z}$ is the free-electron number per atom transferred from the solid to the liquid and calculated using the electrostatic potential energy (17).

| Element | $R^*_{2n} \times 10^{-28}$ | $N_{\Delta z} / V_{m}$ | $M_{\Delta z}^2 \times 10^{28}$ | $v$ | $\Delta U_{V_m}$ | $\Delta H_{m}$ (kJ) | $\Delta z_{F}$ | $\Delta q_{z}$ |
|---------|-----------------|-----------------|-----------------|-----|-----------------|-----------------|-----------------|-----------------|
| Ti      | 2.85            | 5.14            | 105.2           | 1.64 | 0.044           | 15.4            | 0.076           | 0.137           |
| Fe      | 2.54            | 7.57            | 97.2            | 1.38 | 0.054           | 13.8            | 0.078           | 0.109           |
| Co      | 2.35            | 7.93            | 109             | 1.44 | 0.068           | 16.2            | 0.102           | 0.119           |
| Ni      | 2.25            | 8.14            | 126.6           | 1.54 | 0.062           | 17.5            | 0.099           | 0.123           |
| Zn      | 2.45            | 6.06            | 88.7            | 1.42 | 0.046           | 7.3             | 0.065           | 0.056           |
| Pd      | 2.54            | 5.96            | 91.8            | 1.46 | 0.082           | 17.6            | 0.126           | 0.14            |
| Cd      | 2.76            | 4.3             | 87.6            | 1.59 | 0.048           | 6.2             | 0.077           | 0.053           |
| Pt      | 2.56            | 5.84            | 116.1           | 1.65 | 0.069           | 19.7            | 0.120           | 0.157           |
| Au      | 2.66            | 5.53            | 121.2           | 1.74 | 0.057           | 12.6            | 0.102           | 0.105           |
| Al      | 2.49            | 5.33            | 97.8            | 1.56 | 0.074           | 10.7            | 0.117           | 0.083           |
| In      | 3.21            | 3.69            | 102.5           | 1.81 | 0.023           | 3.3             | 0.042           | 0.033           |
| Sn      | 2.7             | 3.54            | 123.2           | 2.01 | 0.033           | 7               | 0.067           | 0.059           |
| Pb      | 3.36            | 3.10            | 108.6           | 1.97 | 0.038           | 4.8             | 0.0743          | 0.050           |

Figure 9. The transferred free-electron number $\Delta z$ per atom determined using two independent methods: (1) $\Delta z_{F}$ is determined from the ultrasound velocity in 13 liquid elements and from the free-volume change $\Delta V_{m} / V_{m}$ at $T = T_m$; (2) $\Delta z_{p}$ is calculated with equation (17) taking $\varepsilon_{m \text{mol}}$ = 0.217, and $R^*_{2n} \times 10^{-28}$ and $\Delta H_{m}$ as given in table 2. The line $\Delta z_{F} \equiv \Delta z_{p}$ is respected despite the experimental spread mainly due to the uncertainty on $\Delta V_{m} / V_{m}$.

from equation (17) are compared in figure 9 and are nearly equal despite a large dispersion of points mainly due to errors on $\Delta V_{m} / V_{m}$; there is no noticeable change when the transition elements are subtracted in figure 9. Equation (17) is then well-founded to relate, in a first approximation, the electronic energy saving $\varepsilon_{60}$ to the number $n \times \Delta z$ of transferred electrons; under these conditions, the potential energy is expected to vary as the radius reverse $1 / R_{\text{mm}}$ because $\Delta E_{F}$ and $\Delta z$ would not have to be dependent on $R_{\text{mm}}$. The unmelted crystals in some cases could only contain 9 atoms; $\varepsilon_{m \text{mol}}$ is strongly reduced as shown by the analysis of the TTT diagrams and as compared with the potential energy $U_{0}$. This could be due to quantum effects reducing $E_{q}$ far below the potential energy [40].

An analogy with the charged-crystal properties imbedded in an inert medium is proposed in the absence of a model for a metal [40–42]. The charge $n \times \Delta z e$ cannot be fully screened inside the crystal because there is a deficit of conduction electrons. A tentative is made in 5–2 to calculate a potential energy $-U_{0}$ by assuming that the first energy level $\varepsilon_{q}$ in such well is equal to $\varepsilon_{q} \times 4 \pi R^{3} / 3$ despite the fact that the weakly-bound free electrons of the melt screen the crystal charge instead of only having one electron bound state in the well. It is assumed that this calculated potential energy $-U_{0}$ is a good approximation for the potential acting on the melt conduction electrons.

5.2. Quantum weakening of the electrostatic energy saving

The potential energy previously defined using (17) is a good approximation for numerous transferred electrons ($n \times \Delta z \gg 1$). There is an opportunity to verify if the first-energy levels of an s-state electron moving in vacuum, in a negative spherical potential well $-U_{0}$, can describe the quantified values proportional to $\varepsilon_{1}$ and approximate the true potential energy in the melt even at low radii. The Schrödinger equation has been written with wave functions only depending on the distance $r$ from the potential centre for s states [40],

$$\frac{1}{r} \frac{d^{2}}{d r^{2}}(r \psi) + k^{2} \psi = 0, \quad \text{where} \quad k = \frac{1}{\hbar} [2 m (U_{0} - E_{q})]^{1/2}.$$  

The quantified solutions $E_{q} = n \varepsilon_{q} \Delta H_{m} / N_{A}$ are given by the $k$ value and by (18) as a function of the potential $U_{0}$ associated with the crystal radius $R = R_{\text{mm}}, n$ increasing with the cube of $R_{\text{mm}}$.

$$\sin k R_{\text{mm}} = \frac{\hbar}{\sqrt{2 m R_{\text{mm}}^{2} U_{0}}} \quad \text{or} \quad U_{0} = \frac{n \Delta z e^{2}}{8 \pi \varepsilon_{0} R_{\text{mm}}^{3}},$$  

$\varepsilon_{q}$ is considered as equal to $\varepsilon_{1}(\theta)$ as a function of $R_{2n}(\theta)$. The corresponding quantity for the potential energy $\varepsilon_{1}(\theta) \times U_{0}(\theta) / E_{0}(\theta)$ per atom is plotted in figure 10 for $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ as a function of $R_{2n}(\theta)$ and compared with $\varepsilon_{1, s}$. The energy saving of a crystal having the critical radius in a metallic melt is slightly reduced by quantum effects as compared with $\varepsilon_{1, s} \times U_{0}[R_{2n}^*(\theta)] / E_{0}[R_{2n}^*(\theta)]$, as shown in figure 10. This weakening is stronger for smaller radii.

Other results of this analysis are given in table 3. The electrostatic potential energy in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$
The potential energy $-U_0$ and the charge excess $\Delta z$ per atom carried by a crystal imbedded in a melt are calculated assuming that the first energy level of an electron moving in vacuum and in a spherical potential $-U_0$ is equal to the energy saving $E_q$ defined using $\varepsilon_{i0}$ and $\varepsilon_{nm}$; $U_0$ is nearly equal to $E_q$ when the crystal radius is equal to its critical value; $E_q$ is strongly reduced by quantum effects when $R \ll R_m$ in very good agreement with the calculated values extracted from the TTT diagrams of several alloys.

| Alloys | Radius (nm) | $n$ atoms | $\varepsilon_{i0}$ | $\varepsilon_{nm}$ | $E_q \times 10^{20}$(J) | $U_0 \times 10^{20}$(J) | $\Delta z$ |
|--------|-------------|------------|-------------------|-------------------|----------------------|---------------------|----------|
| Zr$_{21.7}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ | 0.773 | 119 | 1.54 | 0.91 | 189 | 198 | 0.111 |
| Zr$_{21.7}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ | 0.32 | 8.5 | 1.23 | 13 | 163 | 176 | 0.121 |
| Mg$_{80}$Y$_{20}$Cu$_{25}$ | 0.805 | 99 | 1.03 | 0.93 | 8.8 | 38 | 0.121 |
| Mg$_{80}$Y$_{20}$Cu$_{25}$ | 0.36 | 8.8 | 0.3 | 0.3 | 185 | 192 | 0.0525 |
| Pd$_{41}$Cu$_{27}$Ni$_{10}$P$_{20}$ | 0.632 | 80 | 1.76 | 1.54 | 189 | 198 | 0.111 |
| Pd$_{41}$Cu$_{27}$Ni$_{10}$P$_{20}$ | 0.295 | 8.1 | 0.93 | 1.23 | 175 | 183 | 0.129 |
| Fe$_{50}$B$_{17}$ | 0.9 | 281 | 0.3 | 0.3 | 185 | 192 | 0.0525 |

Table 3. The potential energy $-U_0$ and the charge excess $\Delta z$ per atom carried by a crystal imbedded in a melt are calculated assuming that the first energy level of an electron moving in vacuum and in a spherical potential $-U_0$ is equal to the energy saving $E_q$ defined using $\varepsilon_{i0}$ and $\varepsilon_{nm}$; $U_0$ is nearly equal to $E_q$ when the crystal radius is equal to its critical value; $E_q$ is strongly reduced by quantum effects when $R \ll R_m$ in very good agreement with the calculated values extracted from the TTT diagrams of several alloys.

6. Conclusion

The energy saving $\varepsilon = \varepsilon_{i0} \Delta H_m/V_m$ associated with the equalization of Fermi energies of a crystal and its melt cannot be neglected in the Gibbs free energy change related to a crystal formation in bulk metallic glass-forming melts because it can be larger than its fusion heat. The thermal dependence $\varepsilon_{i0} = \varepsilon_{i00} (1 - \theta/\theta_0)$, where $\theta = T - T_m/T_m$ is found using a thermodynamics constraint that imposes that the derivative of the free-energy change related to a crystal formation at the melting temperature has to be equal to the fusion entropy; this condition is satisfied because $d\varepsilon/dT = 0$ at $T = T_m$. This law has already been observed for undercooled liquid elements.

In bulk metallic glass-forming melts, the homogeneous nucleation critical temperature $T_2$ occurs for $\theta_2 = (\varepsilon_{i0} - 2)/\varepsilon_{i0}$ and the minimum values of $\varepsilon_{i0}$ are only determined with the knowledge of the free-volume disappearance temperature $T_0$ or $\theta_0$; $\theta_2$ is larger than $-2/3$ when $\varepsilon_{i0}$ is larger than 1; in this case, the extrapolated temperature $T_0$, considered as equal to the Vogel–Fulcher–Tammann temperature (VFT); $T_{VFT}$ is larger than $T_m/3$. In conventional glasses, $\varepsilon_{i0}$ is smaller than 1 and $T_0 = T_2 = T_m/3$. The glass-forming ability appears as being strongly dependent on $\varepsilon_{i0}$.

The critical radius for crystal growth in glass melts is much smaller than in pure liquid elements. The steady-state...
Table 4. The abbreviations of different physical quantities used in this paper are classified: (1) Thermodynamics parameters, (2) Physical constants, (3) Glass-forming melt and crystal nucleation parameters, (4) Crystalized nuclei, (5) Temperatures (6) Other abbreviations.

1-Thermodynamic parameters

\begin{itemize}
\item $E_r$: Fermi energy of the melt
\item $-U_0$: Crystal electrostatic potential energy in the melt
\item $\varepsilon_q$: Crystal-quantified electrostatic energy
\item $\varepsilon_{\text{em}}(\theta)$: Equation (2), value of $\varepsilon_{\text{em}}(\theta)$ of unmelted crystals for $R_m < R_{2\Delta m}$, $\varepsilon_{\text{em}}(0) = \varepsilon_{\text{m0}}$
\item $\Delta H_m$: Fusion enthalpy per mole
\item $\Delta S_m$: Fusion entropy per mole
\item $\varepsilon_q$: Crystal-quantified energy saving coefficient in vacuum
\item $\Delta E_F$: Fermi energy difference barrier
\item $E_F$: Fermi level
\item $E_F^{(\text{crystal})}$: Fermi level of the crystal
\item $E_F^{(\text{melt})}$: Fermi level of the melt
\item $\Delta G_{2\Delta m}^*$: Critical energy for crystal growth
\item $\Delta G_{\text{em}}^*_{\text{crit}}$: Contribution of unmelted crystals to the critical energy barrier reduction
\end{itemize}

2-Physical constants

\begin{itemize}
\item $e$: Electron charge
\item $m$: Electron mass
\item $h$: Planck constant; $h = h/2\pi$
\item $N_A$: Avogadro number
\item $k_B$: Boltzmann constant
\item $\epsilon_0$: Vacuum permittivity
\item $M$: Equation (16); Atomic mass
\end{itemize}

3-Glass-forming melt and crystal nucleation parameters

\begin{itemize}
\item $\ln A$: In $A \geq 90 \pm 2$ or $A \geq 10^{19+1}$ m$^{-3}$ s$^{-1}$
\item $K_b$: Equation (9), pre-exponential factor of the nucleation rate $J$
\item $J$: Nucleation rate per unit volume per second
\item $t_{\text{se}}$: Steady-state nucleation time
\item $t_{\text{ns}}$: Time lag in transient nucleation
\item $t$: Equation (12); Crystallization time
\item $t_n$: Crystallization time at the nose temperature $T_n$
\item $N$: Number of atoms per unit volume $N = N_A/V_m$
\item $\Gamma'$: Zeldovich factor
\item $\eta$: Equation (8); Dynamic viscosity (Pa s)
\item $\eta_0$: Equation (8); Pre-exponential factor of the $\eta(\nu)$-T viscosity
\item $D^*$: Equation (8); Fragility parameter
\item $R_v$: Cooling rate (K s$^{-1}$)
\item $R_h$: Heating rate (K s$^{-1}$)
\item $V$: Undercooled melt volume (m$^3$) under processing
\end{itemize}

4-Crystallized nuclei

\begin{itemize}
\item $n$: Number of atoms in a spherical crystal
\item $R$: Crystal radius
\item $R_{s}\Delta m$: Critical radius for crystal growth (calculated with $\varepsilon_{\Delta m}$)
\item $R_{\text{em}}$: Unmelted crystal radius ($m$)
\item $j$: Atom number of the critical size crystal
\item $\sigma_{2\Delta m}$: Surface energy (J m$^{-2}$)
\item $\sigma_{2\Delta m}$: Equations (3) and (6)
\end{itemize}

5-Temperatures

\begin{itemize}
\item $T_m$: Melting temperature
\item $T_l$: Liquidus temperature
\item $T, \theta$: Absolute temperature $T, \theta = (T - T_m)T_m^{-1}$
\end{itemize}

Table 4. continued.

| $T_2, \theta_2$ | Homogeneous nucleation critical temperature $\theta_2 = (T_2 - T_m)T_m^{-1}$ |
|----------------|--------------------------------------------------------------------------------|
| $T_{2\Delta m}, \theta_{2\Delta m}$ | Heterogeneous–nucleation critical temperature $T_{2\Delta m}, \theta_{2\Delta m} = (T_{2\Delta m} - T_m)T_m^{-1}$ |
| $T_{\Delta t}, \theta_{\Delta t}$ | Free-volume disappearance temperature $T_{\Delta t}, \theta_{\Delta t} = (T_{\Delta t} - T_m)T_m^{-1}$ |
| $T_{\text{VFT}}$ | Vogel–Fulcher–Tamman temperature, Equation (10) |
| $T_d, \theta_d$ | Melt crystallization temperature using a heating rate of 0.66 K s$^{-1}$ |
| $T_m$ | Nose temperature of the TTT diagram $T_m, \theta_m = (T_m - T_m)T_m^{-1}$ |

6-Other symbols

\begin{itemize}
\item $v$: Free electron number per atom of the melt
\item $\Delta v$: Variation of $v$ between solid and melt
\item $\Delta \varepsilon$: Equation (14), Free-electron excess per atom above $E_F$
\item $\omega_0$: Equation (16), Ultrasound velocity in the melt at $T = T_m$
\end{itemize}

heterogeneous nucleation rate is strongly dependent on the unmelted intrinsic crystal contribution to the reduction of the critical energy barrier. The time lag in transient nucleation being proportional to the viscosity protects the undercooled melt against crystallization above the glass transition and below the nose temperature of the TTT diagram. The TTT diagrams of Mg$_{54.5}$Y$_{13}$Cu$_{25.5}$, Zr$_{41.2}$Ti$_{13.3}$Cu$_{12.5}$Sn$_{10.0}$Be$_{22.5}$ and Pd$_{43}$Cu$_{25}$Ni$_{10}$P$_{20}$ are calculated in agreement with the experimental ones using known thermodynamic properties and varying the intrinsic nucleus contribution $\Delta G_{\text{em}}/k_B T$ to the reduction of growth critical barrier. The nose temperature $T_n$ depends very weakly on $\Delta G_{\text{em}}/k_B T$ because the TTT curves below $T_n$ are very reproducible [17], the time lag $t_{\text{ns}}$ becoming larger than the steady-state nucleation time $t_{\text{ns}}$. The experimental TTT diagrams are also used to determine, through $\Delta G_{\text{em}}/k_B T$, the value of $\varepsilon_{\text{m0}}$ of intrinsic nuclei and their radii; for radii much smaller than the critical radius, $\varepsilon_{\text{m0}}$ is strongly reduced.

This phenomenon is due to quantum effects associated with electrostatic potentials induced by unmelted spherical crystals in the melt Fermi Sea; the reduced values of $\varepsilon_{\text{m0}}$ correspond in vacuum to the first energy level of one s-electron moving in the same spherical attractive potential despite the fact that, in a metal, the charge screening is built by many-body effects. Such one-electron bound states become virtual in a metal and are characterized by melt conduction electrons surrounding and screening the crystal grain charges.

The first-crystallization temperature of melts is determined on the basis of the existence of intrinsic heterogeneous nuclei that are not melted. The presence of such nuclei is known for many years despite applying relatively large overheating [45–48]; the model can be used to predict a nucleus melting temperature as a function of $\varepsilon_{\Delta 0}$ by overheating the glass-forming melts. Nevertheless, this application is limited to homogeneous compositions and cannot be used for all compositions of crystals surviving in a glass melt.

Medium-range regions have been observed for a long time in an as-quenched conventional glass by studying the...
microstructure of Fe$_{35}$B$_{15}$ amorphous ribbons by several techniques and in particular by high-resolution transmission electron microscopy. The TTT diagram has been calculated to predict a first-crystallization temperature equal to $T_c$; an unmelted crystal radius $R_{\text{unm}}$ equal to 0.9 nm is obtained in agreement with direct observations of the ‘medium range order’ (MRO) region size at room temperature [33]. These regions could be seen as intrinsic unmelted crystals.

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