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► To cite this version:

Robert F Tournier. Thermodynamic and Kinetic Origins of the Vitreous Transition. *Intermetallics*, 2012, 30, 10.1016/j.intermet.2012.03.024 . hal-02937054

HAL Id: hal-02937054

<https://hal.science/hal-02937054>

Submitted on 12 Sep 2020

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Thermodynamic and Kinetic Origins of the Vitreous Transition

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Keywords: 64.70.kj Glasses, 64.70.P Glass Transitions, 64.70pe Metallic Glasses, 64.70ph.
Non Metallic Glasses, 64.70 pj Polymers, 64.60 Q- Nucleation

Abstract:

A unique vitreous transition temperature T_g^* has been recently determined by an extrapolation of the fully-relaxed enthalpy H_r down to zero as a function of temperature. This exothermic heat is linearly decreasing with temperature and the slope dH_r/dT is equal to the specific heat jump from the vitreous to the undercooled state and to the specific heat difference between crystal and melt because a freezing of atom freedom degrees in the liquid state is associated with the vitreous transition at T_g^* . It has been also shown that T_g^* is a material constant which is equal to a crystal homogeneous nucleation temperature in glass-forming melts. A volume energy saving ε_v has been added to the classical Gibbs free energy change $\theta \times \Delta H_m / V_m$ for a crystal formation in a melt where ΔH_m is the fusion heat, V_m the molar volume, $\theta = (T - T_m) / T_m$ and T_m the melting temperature. We show here that ε_v is equal to the Laplace pressure change $(p - p_0)$ as compared to the classical pressure $p_0 = \theta \times \Delta H_m / V_m$ acting on crystals imbedded in a melt. The model is able to strictly predict the precise values of the Vogel-Fulcher-Tamman temperature, the energy saving ε_v , the Laplace pressure p and the ratio T_g^* / T_{0g} of fragile liquids when the equilibrium transition temperature T_g^* is known.

These predictions do not work in strong liquids because there are many possible values of T_g^* when the VFT temperature is known. The viscosity at T_g^* has to be known to predict this temperature. The fragility indexes of fragile glasses and the map of fragility indexes of strong liquids depending on the T_g^* and T_{0g} have been also calculated as a function of T_g^* .

1- Introduction

The debate about the origin of the vitreous state seems to be closed among materials scientists because the freezing of liquid-state below a temperature T_g called the vitreous or glass transition is attributed up to now to a kinetic origin instead of a thermodynamic one in spite of the existence of some specific heat measurements using a stepwise differential scanning calorimetry (DSC) technique which shows that the transition temperature is fixed and only depends on the chemical composition. A reversible specific heat shows a jump at a temperature T_g^* regardless the heating and cooling rates and an exothermic or endothermic heat is relaxed during the relaxation time at temperatures T_g smaller or larger than T_g^* when As_2Se_3 and As_2S_3 samples are annealed at T_g after quenching at lower temperatures [1-3].

We assume that a thermodynamic transition temperature T_g^* exists among the time dependent transition temperatures T_g in glass formers which does not depend on the heating and cooling rates and we look at some consequences of this assumption. A relaxation time τ exists at any temperature around T_g^* ; τ increases when the temperature decreases and is viewed as a time-lag in crystal transient nucleation necessary to induce the transformation of an undercooled fragile liquid in a frozen vitreous state [4]. The sample can be quenched in the undercooled state down to temperatures T_g lower than T_g^* as shown in Figure 1. A transformation in an equilibrium state occurs at any temperature smaller or larger than T_g^*

and is accompanied by a relaxed enthalpy which does not depend on time when it is saturated. The relaxation time has to be much longer than the time necessary to homogenize the temperature inside the sample before starting the enthalpy measurement. The fully-relaxed enthalpy H_r at T_g is equal to the surface ABCD in Figure 1 when the sample has been cooled down to this temperature. The enthalpy H_r is an endothermic heat equal to the surface CDEF when the sample is heated from the vitreous state to a temperature T_g larger than T_g^* . The following equation applied to fragile glass-forming melts is obeyed:

$$H_r = \int_{T_g}^{T_g^*} \Delta C_{p_{gl}} dT \quad (1)$$

where $\Delta C_{p_{gl}}$ is equal to the specific heat difference $C_{pl}-C_{pg}$ between the undercooled and vitreous or crystallized states in agreement with a whole freezing of the melt [4]. This description is based on the assumption that the relaxation time is, in fact, a time-lag related to transient homogeneous nucleation. It is corroborated by the viscosity increase with time towards the equilibrium of the vitreous state at temperatures smaller than T_g^* because we expect that the viscosity in the vitreous state has to be larger than the one in the undercooled quenched melt [5-7].

An endothermic heat bump depending on the heating rate characterizes the transition glass-melt at T_g when the vitreous transition is determined with a technique of differential scanning calorimetry (DSC) without any anomaly at T_g^* . It can be deduced that the exothermic heat ought to be a linear function of the temperature and then $\Delta C_{p_{gl}}$ cannot depend on temperature. The vitreous transition T_g^* would be defined, in this description, at the disappearance temperature without any anomaly at T_g^* . The disappearance temperature T_g^* of the relaxed enthalpy is obtained, in these conditions, using a linear extrapolation of H_r down to zero. The T_g^* would separate the frozen and undercooled states.

The fully-relaxed enthalpies of $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$, glycerol, $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ and As_2Se_3 are linear functions of T [4]; the thermodynamic transition temperature T_g^* exists and has been extrapolated from the measurements of the fully-relaxed enthalpy. A reversible specific heat jump is observed in As_2Se_3 at the same temperature T_g^* with a stepwise DSC technique regardless the cooling and heating rates [1-3]. The specific heat jump of As_2Se_3 calculated from (1) is equal to the measured one in perfect agreement with the description given in Figure 1. ΔC_{lg} is a little smaller in the other glass-forming melts than that measured by DSC because of the existence of a residual endothermic contribution.

The idea of a thermodynamic transition T_g^* is so much rejected that the disappearance temperature of the relaxed enthalpy is never used to determine the glass transition in spite of the fact that this quantity does not depend on time when it is saturated. The equilibrium viscosity values $\eta(T)$ below T_g are also considered, up to now, as belonging to the undercooled state because the vitreous state is viewed as a continuous prolongation of the liquid state at lower temperatures. A continuous Vogel-Fulcher-Tammann law given by (2) including values below and above T_g is used to determine the VFT temperature T_0 and the fragility index D^* [5-7]:

$$\eta = \eta_0 \exp\left(\frac{D^* T_0}{T - T_0}\right). \quad (2)$$

This analysis tends to deny the observation of a phase transition using the viscosity measurement. Nevertheless, an increase of viscosity exists during the relaxation time which is the time lag for the formation of a cluster distribution. The viscosity values of the quenched state belong to the undercooled state and the equilibrium viscosity to the frozen vitreous state. The reversible specific heat measurement however indicates that the transition always occurs

at the same temperature T_g^* while the exothermic heat depends on the temperature of annealing. This transformation of the undercooled melt in a frozen state at any temperature T_g would only produce an exothermic heat while the equilibrium reversible transition of fragile liquids would always occur at T_g^* because there is a minimum of the energy saving at this temperature [1-3].

The relaxation times are too long to be related to a first or second order phase transition. They have to be associated with a crystal nucleation temperature leading in a first step to a vitreous phase on the long way to a crystallized phase. The transient homogeneous nucleation time to form a cluster distribution and the steady-state nucleation time all together lead to unattainable time lags before the occurrence of a homogeneous crystallization [8]. The Gibbs free energy change $\theta \times \Delta H_m / V_m$ associated with a cluster formation in a melt has to be increased to reflect the volume energy saving ε_v associated with Fermi energy equalization of nascent crystals and melts. The reduced temperature θ is equal to $(T - T_m) / T_m$, T_m the melting temperature, ΔH_m the fusion heat per mole and V_m the molar volume [9-13]. A similar proposal has been made for crystal formation in metallic and nonmetallic melts because the chemical potential of a small cluster ought to differ from the bulk value in presence of a density difference between cluster and melt and of a Laplace pressure p added to the classical pressure p_0 of the melt [14]. The energy saving as compared to $\theta \times \Delta H_m$ would be equal to $(p - p_0) \times V_m$. We have recently shown that these two quantities are equal for titanium at the melting temperature [15].

The energy saving coefficient $\varepsilon_{ls} = \varepsilon_v / \Delta H_m \times V_m$ is a function of θ^2 ; ε_{ls} is equal to a maximum value ε_{ls0} at T_m corresponding to the maximum of the Fermi energy difference and to zero at $\theta = \theta_{0g}$ where θ_{0g} is equal to the Vogel-Fulcher-Tammann temperature which corresponds to the free-volume disappearance temperature [9,10]. Metallic clusters formed in

a liquid element with a radius smaller than the critical one has a one-particle-density of states of s state electrons disappearing at low radius. The energy saving associated with cluster radii smaller than 0, 5 nanometer is a quantified quantity which leads to a conduction gap opening. The same size-dependent changes in the electronic structure of metal clusters in vacuum have been observed by scanning tunneling spectroscopy. Metallic clusters in melts have the same properties than in vacuum [15]. The new crystal nucleation temperature θ_{2ls} is equal to $(\epsilon_{ls} - 2)/3$ instead of $-2/3$ as predicted by the classical nucleation model with $\epsilon_{ls} = 0$. These two relations have to be respected at the homogeneous nucleation temperature and lead to a quadratic equation that has been used to determine θ_{2ls} as a function of ϵ_{ls0} and θ_{0g} [9,11]. The Angell's description in terms of strong and fragile glass-forming melts is found when we assume that the vitreous transition occurs at the homogeneous nucleation temperature of glass-forming melts. The quadratic equation solutions have been used to determine, in agreement with many experimental results, the relations between the VFT temperatures T_{0g} governing the temperature dependence of relaxation time of many melts, the vitreous transition T_g^* and the energy saving coefficient ϵ_{ls0} at T_m .

The quantified energy savings of crystals having a radius equal or smaller than the critical one depends on the number of s state electrons which are transferred from a nascent crystal to the melt. A spherical attractive potential energy is created which is screened in the melt by conduction electrons; ϵ_{ls0} at $T = T_m$ is quantified, depends on the crystal radius R_{nm} and corresponds to the first energy level of one-s electron moving in vacuum in the same spherical attractive potential despite the fact that the charge screening is built by many-body effects [9,11,15]. The existence of an energy saving ϵ_v has for consequence that some crystals having a radius smaller than the critical one survive above T_m , act as growth nuclei in undercooled melts and produce crystallization at temperatures much higher than the

homogeneous nucleation temperature when the cooling rate is too weak. These quantified values of ε_{ls0} have been used to predict the undercooling temperatures of gold and titanium in perfect agreement with experiments [15,16].

This model is used here to describe the energy saving variation when the glass transition temperature T_g is varied near the thermodynamic transition T_g^* of several glass-forming melts. Several maps are established which represent T_g^*/T_{0g} versus the reduced glass transition temperature θ_g^* , the energy saving coefficients ε_{ls0} of strong and fragile glasses versus θ_g^* . The energy saving coefficient ε_{ls0} is always larger in fragile glass-forming melts than that of strong melts.

We also show, for the first time, that the quantity $(p-p_0) \times V_m / \Delta H_m$ is equal to the energy saving coefficient ε_{ls0} per mole at the melting temperature and to ε_{ls} down to T_g regardless of melts. It explains why this model can be used in nonmetallic glass-forming melts [4].

2- The Gibbs free energy change associated with crystal formation in melts is completed by an energy saving

Transformations liquid-solid always induce changes of the conduction electron number per volume unit, and sometimes per atom. The equalization of Fermi energies of a spherical particle containing n atoms having a radius R smaller than a critical value $R_{2ls}^*(\theta)$ and of its melt produces an unknown energy saving ε_v per volume unit. The ε_v value is equal to a fraction ε_{ls} of the molar fusion heat ΔH_m per molar volume V_m . This energy has been included in (3) which is the Gibbs free energy change $\Delta G_{2ls}(\theta)$ associated with a crystal

formation in metallic melts, θ being equal to $\theta = (T-T_m)/T_m$ and T_m the melting temperature [9-13];

$$\Delta G_{2ls}(R, \theta) = \frac{\Delta H_m}{V_m}(\theta - \varepsilon_{ls})4\pi \frac{R^3}{3} + 4\pi R^2 \frac{\Delta H_m}{V_m} \left(\frac{V_m}{N_A}\right)^{1/3} \alpha_{2ls} \quad (3)$$

where

$$\alpha_{2ls} = (1 + \varepsilon_{ls}) \left[\frac{N_A k_B \ln(K_{ls})}{36\pi \Delta S_m} \right]^{1/3}, \quad (4)$$

$$\ln(J \cdot v \cdot t_{sn}) = \ln(K_{ls} \cdot v \cdot t_{sn}) - \left[\frac{\Delta G_{2ls}^* - \Delta G_{nm}}{k_B T} \right], \quad (5)$$

$$\ln(K_{lgs}) = \ln\left(\frac{A \eta_0}{\eta}\right) = (\ln A) \pm 2 - \frac{B}{(T - T_{0g})}, \quad (6)$$

$$\frac{\Delta G_{2ls}^*}{K_B T} = \frac{12}{81} \frac{(1 + \varepsilon_{ls})^3}{(\theta - \varepsilon_{ls})^2} \frac{\ln K_{ls}}{(1 + \theta)} \quad (7)$$

$$R_{2ls}^*(\theta) = -\alpha_{2ls} \frac{2}{\theta - \varepsilon_{ls}} \left(\frac{V_m}{N_A}\right)^{1/3} \quad (8)$$

N_A is Avogadro's number, k_B Boltzmann's constant, ΔS_m in (4) the fusion entropy, J in (5) the nucleation rate, ΔG_{2ls}^* the critical energy barrier of crystal growth given by (7), R_{2ls}^* the growth critical radius given by (8), v the sample volume, t_{sn} in (5) the steady-state nucleation time, T_{0g} in (5) the disappearance temperature of the free-volume in glass-forming melts having a viscosity following a Vogel-Fulcher-Tammann law [17]; $\ln A$ in (6) is equal to 90 in liquid elements and to about 100 at the vitreous transition T_g when K_{ls} in (5) and (6) is defined in $m^{-3} \cdot s^{-1}$ [4,9,18] ; $B/(T_g - T_{0g})$ in (6) is equal to 36 (see 7-). The contribution of unmelted crystals (clusters) of radius R_{nm} to the reduction of the critical energy barrier is given by (3)

with $R = R_{nm}$ being constant and equal to R_{nm} when T decreases down to a temperature for which $\Delta G_{eff}/k_B T = \Delta G^*_{2ls}/k_B T - \Delta G_{nm}/k_B T$ in (5) becomes equal to $\ln K_{ls}$ [8,19]. The classical equations $\Delta G_{1ls}(\theta)$ and α_{1ls} are obtained with $\varepsilon_{ls} = 0$ [18,19]. The experimental values of α_{1ls} and of the lowest undercooling temperatures have been used to determine α_{2ls} and ε_{ls} [10,18]. The thermal variation of ε_{ls} is an even function of θ given by (9) where $\theta_{0g} = (T_{0g} - T_m)/T_m$ [9,10]; then, the fusion heat of unmelted crystals remains equal to ΔH_m regardless of their radius.

$$\varepsilon_v = \varepsilon_{ls} \frac{\Delta H_m}{V_m} = \varepsilon_{ls0} \left(1 - \frac{\theta^2}{\theta_{0g}^2}\right) \frac{\Delta H_m}{V_m} \quad (9)$$

The derivative $dJ/d\theta$ is proportional to $(3\theta - \varepsilon_{ls} + 2)$ when $\Delta G_{nm} = 0$ [10]; the homogeneous nucleation temperature T_{2ls} is given by (10) when $(3\theta - \varepsilon_{ls} + 2) = 0$; at $T = T_{2ls}$, we have in (5) $J = 1 \text{ m}^{-3} \text{ s}^{-1}$, $v \cdot t_{sn} = 1$, $\ln(J \cdot v \cdot t_{sn}) = 0$ and $\ln K_{ls} = \Delta G^*_{2ls}/k_B T_{2ls}$:

$$\theta_{2lps} = \frac{(T_{2ls} - T_m)}{T_m} = \frac{\varepsilon_{ls} - 2}{3} \quad (10)$$

We apply these equations to glass-forming melts assuming that the glass transitions occurs at $T_g^* = T_{2ls}$ (or $\theta_g = \theta_{2ls}$) [4].

3- The crystal homogeneous nucleation temperature and the vitreous transition

The crystal growth critical energy ΔG^*_{2ls} given by (1) divided by $\ln K_{ls}$ is plotted in

Figure 2 as a function of the reduced temperature θ using several values of ε_{ls0} covering the entire window of bulk glass- forming melts. The homogeneous nucleation temperature θ_{2ls} occurs at temperatures increasing with ε_{ls0} . The equality $\Delta G^*_{2ls} \cong \ln K_{ls}$ is respected in a broad window of temperatures above the nucleation temperatures; θ_{2ls} strictly depends on the energy saving which increases with ε_{ls0} and θ_{0g} as shown by (9) while $\ln K_{ls}$ depends on the temperature in (6) through the viscosity [8]. The crystal homogeneous nucleation temperature is also determined by kinetic effects through $\ln K_{ls}$. The relaxation time is viewed as the transient nucleation time τ^{ns} given by (11) :

$$\tau^{ns} = \frac{\pi N}{12\Gamma \times K_{ls}} = \frac{\pi N}{12} J_c \left(\frac{3\pi}{\ln K_{ls}} \right)^{1/2} \exp(-\ln A) \times \exp\left(\frac{B}{T - T_{0g}}\right) = \tau_0 \exp\left(\frac{B}{T - T_{0g}}\right) \quad (11)$$

where Γ is Zeldovitch's factor, $N = N_A/V_m$, J_c the atom critical number for steady-state nucleation [8]. The value of τ^{ns} at the vitreous transition viewed as a crystal homogeneous nucleation temperature is of the order of 100 seconds. The pre-exponential factor τ_0 is proportional to $T_g/\Delta H_m/V_m \times \ln K_{ls}/K_{ls}$ with $T_g/\Delta H_m$ being nearly the same in all melts. We deduce that $\ln K_{ls}$ is equal to 62.5 ± 2 , $\ln A = 98.5 \pm 2$ with $B/(T_g - T_{0g}) = 36$ in all undercooled melts at T_g^* (see 5-), K_{ls} and A in $m^{-3} \times s^{-1}$ with $B = T_{0g} \times D^*$ in (2) and (6) and D^* the fragility index [4,20,21].

The nucleation temperature θ_{2ls} occurs not only at a precise value of the energy saving coefficient ε_{ls0} but also when $\ln K_{ls}$ becomes equal to 62.5 ± 2 [4]; kinetic and thermodynamic effects are combined to produce the vitreous transition; nevertheless, θ_{2ls} may exist without being a vitreous transition when $D^*T_0/(T_{2ls} - T_{0g})$ cannot be equal to 36, $\ln K_{ls}$ is much larger than 62.5 in many liquid elements and the viscosity remains too small in spite of an Arrhenius behavior.

4- Fragile glass-forming melts

Equations (9) and (10) are applied at $T = T_{2ls}$ (or $\theta = \theta_{2ls}$); the quadratic equation (12) is obtained:

$$\frac{\theta_{2ls}^2 \varepsilon_{ls0}}{\theta_{0ls}^2} + 3\theta_{2ls} + 2 - \varepsilon_{ls0} = 0 \quad (12)$$

There are two values of θ_{2ls} given in (13) which are solutions of (12) for each value of θ_{0g} and ε_{ls0} respectively larger than $-2/3$ and 1 [9,11]; they correspond to fragile glass-forming melts and are out-of-equilibrium values:

$$\theta_{2ls} = \frac{-3 \pm [9 - 4(2 - \varepsilon_{ls0})\varepsilon_{ls0} / \theta_{0g}^2]^{1/2}}{2\varepsilon_{ls0}} \theta_{0g}^2 . \quad (13)$$

The minimum value of ε_{ls0} is obtained when (14) and (15) are respected:

$$\varepsilon_{ls0} = \varepsilon_{ls}(\theta=0) = 1.5 * \theta_{2ls} + 2 \quad (14)$$

$$\theta_{0ls}^2 = \frac{8}{9} \varepsilon_{ls0} - \frac{4}{9} \varepsilon_{ls0}^2 \quad (15)$$

The coefficients ε_{ls0} of four fragile glass-forming melts N°1, 2, 3 and 5 are represented in Figure 3 as a function of θ_{2ls} assuming that θ_{2ls} is equal to θ_g [22,7,23,5,6]; the transition at

equilibrium is given by (14) and represented by a straight line; the various parameters characterizing these melts are given in Table 1.

The ratios T_g^*/T_{0g} have been calculated using (14) and (15) and are compared with the experimental results in Table 1 and Figure 4. We assume in the calculation of T_g^* that the six melts are fragile. The melts N°4 and N°6 are not following the equations (14) and (15) of fragile melts in spite of the fact that their experimental reduced temperature θ_{0g} is a little larger than $-2/3$. Their vitreous transition is much larger than the expected value for a fragile melt. The experimental values T_{0g} of N°6 and of N° 4 are a little large because of experimental errors. The other melts N°1, N°2, N°3 and N°5 are fragile; their glass transition corresponds to the thermodynamic transition and to the minimum of ϵ_{ls0} represented in figure 3. A glass transition of 622 K and an energy saving coefficient $\epsilon_{ls0} = 1.229$ are calculated from (13) with $T_{0g} = 356$ K which corresponds to $\theta_{0g} = -2/3$ assuming that the melt N° 6 is strong. The same ratio T_g^*/T_{0g} is plotted as a function of θ_{0g} in Figure 5; it strongly varies when θ_{0g} is very close to $-2/3$. The vitreous transition of fragile liquids tends to be equal to the free-volume disappearance temperature.

The fragile liquids have an equilibrium homogeneous nucleation temperature θ_{2ls} that only depends on ϵ_{ls0} and does not strictly depend on $\ln K_{ls}$ and then on the viscosity even if $\ln K_{ls}$ has a value nearly equal to 62.5 at this temperature. The kinetic character of the vitreous transition $\theta_{2ls} = \theta_g^*$ is accompanying the thermodynamic vitreous transition at equilibrium because the freezing of atom freedom degrees is produced by a well-defined value of $\ln K_{ls}$ which is T_g^* dependent through $[D^*T_{0g}/(T_g^*-T_{0g})]$ and also through $\ln A$.

5- Strong glass-forming melts

The energy saving coefficient ε_{ls0} of strong glass-forming melts is calculated using (13) when $\theta_{2ls} = \theta_g^*$ and $\theta_{0g} < -2/3$ are known. There is a boundary $\theta_{0g} = -2/3$ (or $T_{0g} = T_m/3$) that separates strong and fragile undercooled liquids in Angell's classification [20]. The coefficient ε_{ls0} is calculated with (13) and is plotted in Figure 6 as a function of $\theta_g^* = (T_g^* - T_m)/T_m$ for various values of θ_{0g} . It varies from 0.217, which is the energy saving coefficient of liquids elements, up to 2. The nucleation reduced temperature θ_g^* increases from $-2/3$ up to zero and corresponds to many possible values of the vitreous transition. It has been shown that T_g strongly depends on the heating rates; the homogeneous nucleation temperature θ_{0g} can exist without leading to a vitreous transition because $\ln K_{ls}$ in (6) is not always equal to equal to 62.5 [4-6].

The largest values of ε_{ls0} correspond in Figure 6 to fragile melts and are aligned on a straight line while the ε_{ls0} of strong melts is smaller and decreases when θ_{0g} tends to -1 with the increase of the Arrhenius character of the VFT law. Liquids are called strong because they are more resistant to structural change than fragile liquids [20]. The VFT temperature of fragile glasses near the maximum of T_g/T_{0g} is equal to about $0.65 \times T_g$ and increases up to $0.77 \times T_g$ at higher temperatures while $-0.5 \times \theta_g$ has to be added to $\varepsilon_{ls0}(\theta_g)$ [4]. These changes of the VFT temperature and the energy saving also characterize the fragile liquids and would be related to a decrease of the Fermi energy difference between crystal and melt when the temperature decreases. This change could be present or absent in the strong ones.

The thermodynamic vitreous transition T_g^* of a strong melt continuously increases with ε_{ls0} for a given value of θ_{0g} as shown in figure 6. A strong glass has a relaxation time which follows a VFT law around the vitreous transition [6]. The true T_g^* can be determined by studying the thermal variation of the fully-relaxed enthalpy and the value of ε_{ls0} can be

deduced from the knowledge of T_g^* and T_{0g} using (13). A unique value of T_g^* is also expected in each strong melt in spite of the existence of many possible homogeneous nucleation temperatures because T_g^* is probably fixed by a unique and universal value of viscosity at this temperature.

6- Is the viscosity a universal quantity accompanying the vitreous transition?

The thermodynamic vitreous transition T_g^* of a strong melt continuously increases with ε_{ls0} for a given value of θ_{0g} as shown in Figure 6. A strong glass has a relaxation time which follows a VFT law around the vitreous transition [6]. The true T_g^* can be determined by studying the thermal variation of the fully-relaxed enthalpy and the value of ε_{ls0} can be deduced from the knowledge of T_g^* and T_{0g} using (13). A unique value of T_g^* is then expected in each strong melt in spite of the existence of many possible homogeneous nucleation temperatures because T_g^* is probably fixed by a unique and universal value of viscosity at this temperature.

7- The fragility indexes of strong and fragile liquids

The relation (16) is used to calculate the fragility indexes which results from the fact that $[D^*T_{0g}/(T_g^*-T_{0g})]$ is considered, up to now, as being equal to 36-39 [20,21]. The constant 36 is used to calculate the fragility indexes of liquids when T_g/T_{0g} is known; It is deduced from the average value of the proportionality coefficient of D^* with $(T_g^*/T_{0g}-1)$ [22]:

$$\frac{T_g^*}{T_{0g}} \cong 1 + \frac{D^*}{36} \quad (16)$$

The ratio T_g^*/T_{0g} of strong and fragile liquids is calculated using (13) and (14) respectively. The fragility indexes of fragile and strong liquids deduced from (16) are plotted as a function of ε_{ls0} in Figure 7. A unique value of D^* or T_g^*/T_{0g} corresponds to ε_{ls0} in fragile liquids while an infinity of values of D^* and T_g^*/T_{0g} corresponds in strong liquids to each value of ε_{ls0} . This point has been already discussed in 5-.

8- The energy saving and the Laplace pressure associated with clusters in melts

It has been already recognized that a volume energy equal $-(p-p_0) \times V_m$ has to be added to the classical Gibbs free energy change $\theta \times \Delta H_m / V_m$ associated with cluster formation in melts in order to reflect the presence of inhomogeneous pressure due to the Laplace pressure p acting on compressible out-of-equilibrium clusters. This proposal can be applied to cluster formation in nonmetallic liquids. In our case, the Fermi energy difference depends on temperature and progressively disappears when the free volume of the melt tends to zero. We have already shown that the saving energy of titanium clusters per mole at the melting temperature T_m is equal to $(p-p_0)V_m$ where p is the Laplace pressure and p_0 the pressure of the melt where p is defined by $p = 2 \times \sigma / R_{2ls}^*$, σ being the cluster surface energy and R_{2ls}^* the critical radius. The pressure p can be calculated from (3,8) and we obtain (17):

$$p = \frac{2 \times \sigma}{R_{2ls}^*} = \frac{\Delta H_m}{V_m} [\theta - \varepsilon_{ls}(\theta)]. \quad (17)$$

The product $(p-p_0) \times V_m = \Delta p \times V_m$ is equal to the saving energy per mole and $p_0 = \theta \times \Delta H_m / V_m$ is the classical contribution which does not depend on the free volume. The energy saving $\varepsilon_{ls} \times \Delta H_m / V_m$ is also the change in the Laplace pressure that we have introduced in (3) ignoring that D. T. Wu, L. Granasy and F. Spaepen had already suggested that an energy $-(p-p_0)V_m$ ought to be added in the classical equation of the Gibbs free energy change for a crystal formation [14]. The Laplace pressure change Δp tends to zero with the cluster radius and with the free volume not only in metallic glass-forming melts but also in nonmetallic glass-forming melts because the equations (9) and (10) are followed by the two types of melts [4,15].

9- Conclusion

The vitreous transition temperature T_g^* has been recently viewed as a material constant which is equal to the crystal homogeneous nucleation temperature in glass-forming melts. This result has been obtained by adding a volume energy saving ε_v per volume unit to the classical Gibbs free energy change $\theta \times \Delta H_m / V_m$ for a crystal formation in a melt. We have shown that ε_v is equal to the experimental Laplace pressure change $(p-p_0)$ as compared to the classical pressure $p_0 = \theta \times \Delta H_m / V_m$ acting on crystals imbedded in a melt. It is now easier to understand why this model also works for nonmetallic glass-forming melts because such inhomogeneous pressure is acting on all crystals having a radius smaller or equal to the critical one.

We have also shown that the model is able to strictly predict the precise value of the Vogel-Fulcher-Tamman temperature, the energy saving ε_v and the ratio T_g^* / T_{0g} of fragile liquids when the equilibrium transition temperature T_g^* is known. These predictions are not

possible in strong liquids because there are a lot of possible values of T_g^* when the VFT temperature T_{0g} is known. The viscosity at T_g^* has to be fixed to determine T_{0g} . The fragility indexes of fragile glasses and the map of fragility indexes of strong liquids depending on the T_g^* and T_{0g} have been calculated as a function of T_g^* .

The vitreous transition temperature T_g^* of all glass-forming melts strictly depends on a precise value of the energy saving at the melting temperature and is accompanied by a freezing of supplementary freedom degrees of atoms in melts as compared to those in crystals. This whole freezing is probably produced by a universal value of the liquid viscosity accompanying the preliminary step of transient nucleation leading to crystallization at unattainable times.

Acknowledgments

This work was sponsored by the Laboratory for the Application of Superconductors and Magnetic Materials involving the Northwest Institute for Non-ferrous Metal Research (NIN), the Northwestern Polytechnical University (NPU) in Xi'an (P.R. China). Thanks are due to Lian Zhou for NIN support as, Dr Jinna Mei from NPU and J.L. Soubeyroux from CNRS/CRETA for their study of relaxed enthalpy of some glass-forming melts [26].

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Figure and Table Captions

Figure 1: The specific heat difference between liquid and vitreous states is plotted versus temperature. The undercooled liquid is quenched down to B at a temperature T_{g1} smaller than the thermodynamic transition T_g^* . The transformation time from the quenched undercooled melt to the vitreous state is equal to the relaxation time and occurs from B to C at T_{g1} accompanied by an exothermic heat equal to the surface ABCD. The sample is rapidly heated up to E; the transformation time from the vitreous to the liquid state is equal to the relaxation time at the temperature T_{g2} and the endothermic heat is equal to the surface ADEF.

Figure 2: The ratio $\Delta G_{2ls}^*/k_B T / \ln K_{ls}$ given by (7) is plotted versus $\theta = (T - T_m)/T_m$ down to $\theta = \theta_{2ls}$ when ϵ_{ls0} given by (9) is equal to 1.8, 1.6, 1.4, 1.2 and 1. It is always equal to 1 far above the homogeneous nucleation temperature θ_{2ls} .

Figure 3: The minimum value of the energy saving coefficient ϵ_{ls0} at the melting temperature T_m follows the linear equation $\epsilon_{ls0} = 1.5 \times \theta_g + 2$ as a function of $\theta_{2ls} = \theta_g = (T_g - T_m)/T_m$. The other values of θ_{2ls} are also solutions of (12). The melts N°1, 2, 3 and 5 are respectively $Pd_{43}Ni_{10}Cu_{27}P_{20}$, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ and $Zr_{65}Al_{10}Ni_{10}Cu_{15}$. Their properties are given in Table 1.

Figure 4: The theoretical values of T_g^* divided by T_{0g} noted A are plotted versus the theoretical value of θ_g^* . Experimental values of T_{0g} have been used to calculate the theoretical values of T_g^*/T_{0g} noted B and given in Table 1 assuming that these melts are fragile. The

points noted C are the experimental values T_g/T_{0g} . The following melts $Mg_{65}Cu_{25}Y_{10}$ and $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ would be strong with a smaller value of T_{0g} .

Figure 5: The theoretical values of T_g^*/T_{0g} divided by T_{0g} noted A are plotted versus θ_{0g} . The experimental quantities T_g^*/T_{0g} noted B and given in table 1 are plotted versus θ_{0g} instead of θ_g^* in Figure 4. This diagram shows that T_g^*/T_{0g} in fragile liquids is strongly varying near $\theta_{0g} = -2/3$. Any experimental uncertainty on T_{0g} leads to a large variation of T_g^* . The points noted C correspond to the experimental values T_g/T_{0g} . The following melts $Mg_{65}Cu_{25}Y_{10}$ and $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ could be strong with a value of T_{0g} being a little smaller.

Figure 6: The energy saving coefficient ε_{ls0} of fragile melts is represented by a straight line as a function of $\theta_g^* = (T_g^* - T_m)/T_m$. Its lowest value 0.217 corresponds to liquid elements. Each curve corresponds to values of θ_g^* equal to $-2/3$, -0.7 , -0.8 , -0.9 and -1 .

Figure 7: The fragility indexes of fragile glasses are distributed along an arc. Strong liquid indexes are calculated for various values of θ_{0g} : $-2/3$, -0.7 , -0.8 -0.9 and -1 .

Table 1: The references for the VFT temperatures T_{0g} are: [22] for N°1, [7] for N°2, [23] for N°3, [5] for N°4, [22] for N°5 and [6] for N°6. The energy saving coefficients ε_{ls0} and T_g^* are calculated with (14) and (15) using the experimental value T_{0g} considering that all these undercooled melts could be fragile; T_g^* or θ_g^* is the thermodynamic transition temperature of fragile melts; the ratios T_g^*/T_{0g} are indicated as a function of $\theta_g^* = (T_g^* - T_m)/T_m$; the temperature T_g is the experimental transition temperature. The experimental ratios T_g/T_{0g} can be compared to the theoretical ones T_g^*/T_{0g} . The experimental fragility indexes D^* are given in the last column.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1

N°	melt	T _m	T _{0g}	ε _{ls0}	T _g [*]	θ _g [*]	T _g [*] /T _{0g}	T _g	T _g /T _{0g}	D [*]	ref
1	Pd ₄₃ Ni ₁₀ Cu ₂₇ P ₂₀	802	365	1.577	576	-0.545	1.58	578	1.58		[24,22]
2	Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni ₁₀ Be _{22.5}	937	396	1.501	625	-0.577	1.58	622	1.57	23.8	[25,22]
253	Zr _{58.5} Cu _{15.6} Ni _{12.8} Al _{10.3} Nb _{2.8}	1110	437	1.415	673	-0.606	1.54	673	1.51	19.7	[23,22]
4	Mg ₆₅ Cu ₂₅ Y ₁₀	739	260	1.234	362	-0.648	1.39	428	1.65	22.1	[5,22]
5	Zr ₆₅ Al ₁₀ Ni ₁₀ Cu ₁₅	1161	437	1.353	660	-0.624	1.51	641	1.47	16.5	[22]
6	Zr _{46.75} Ti _{8.25} Cu _{7.5} Ni ₁₀ Be _{27.5}	1070	372	1.225	504	-0.652	1.67	622	1.67	22.7	[6,22]