

FROM GLASS TO GLASS CERAMICS VIA PHASE TRANSFORMATIONS

Edgar Dutra Zanotto

DEMa - UFSCar

13560 - São Carlos-SP

ABSTRACT

By means of classical nucleation theory and published kinetic (viscosity) and thermodynamic data, calculations were carried out for transient times, τ , steady state nucleation rates, I^0 , temperatures of maximum nucleation rates, T_{\max} , and critical nuclei size for 12 glass forming systems. Two distinct regions were found: For low values of T_g ($T_g/T_f < 0.58$) the temperatures of maximum nucleation rates are at or higher than T_g and the transient times are short, $\tau < 1$ day. Glasses in this region exhibit homogeneous nucleation. For high values of T_g ($T_g/T_f > 0.72$), $T_{\max} < T_g$ and transient times are very long. This could explain the lack of observable homogeneous nucleation in the latter systems if I^0 and the growth rates are reasonable. Albite and B_2O_3 , which are extremely difficult to crystallize, show the longest induction periods ($1 < \tau < 10^{10}$ years). For intermediate values of T_g ($0.59 < T_g/T_f < 0.66$) T_{\max} lie either above or below T_g and transient times vary from hours to years. There is no defined trend for the magnitude of the estimated nucleation rates with increasing T_g . The critical nuclei size at T_{\max} correspond to 6-60 unit cells. The present calculations allow one to predict whether a given system is appropriate for glass ceramic formation.

INTRODUCTION

Glass ceramics are polycrystalline materials obtained by the controlled crystallization of certain glasses which have unusual microstructures (are pore-free and have extremely small grains uniformly dispersed within the matrix phase) and properties. These products show increasingly expanding applications in high-tech industries. To synthesize glass-ceramics, however, one has to induce crystal nucleation in the bulk of the specimen and to minimize surface nucleation. This can only be accomplished through the understanding and control of the crystallization kinetics of glassy materials.

Basic research on phase transformation kinetics in glasses at Federal University of São Carlos initially concentrated on phase separation kinetics and its effects on crystal nucleation and growth [1-8]. Concurrently, experimental tests were carried out for both Classical Nucleation Theory (CNT) and Johnson-Mehl-Avrami Theory [9-12]. More recently, considerable attention is being devoted to the study of surface nucleation [13].

In a recent publication [14] the present author addressed the problem of internal (homogeneous) versus surface (heterogeneous) nucleation in oxide glasses. By comparing calculated and experimental data it was demonstrated that both CNT and ANT (Adiabatic Nucleation Theory), recently developed by Meyer [15], predict very well the temperatures of maximum nucleation rates, T_{\max} . It was also shown that $T_g/T_f < 0.58$ and $T_{\max} > T_g$ for systems which show homogeneous nucleation and vice versa. It was postulated that glass systems with $T_{\max} < T_g$ show only surface nucleation due to long induction times to establish steady state homogeneous nucleation.

Although the above mentioned findings are interesting per se, further questions remain as no quantitative predictions and corresponding experimental evidence for transient times were presented in [14], as pointed out by Meyer [16]. Criteria to experimentally observe homogeneous nucleation, i.e. for homogeneous nucleation to be dominant over heterogeneous nucleation will be assumed to be: i) The steady state homogeneous nucleation frequency must be sufficiently high ($I^0 > 10^3 \text{ m}^{-3} \text{ s}^{-1}$); ii) The transient times τ must be reasonably short ($\tau < \text{few days}$) in the temperature range (ΔT_n) where I^0 is detectable and; iii) a) The crystal growth rates, U , at T_n must be high enough as to allow growth of nuclei to measurable sizes, or, b) U is small but there is a range of higher temperatures where additional growth leads to observable crystals. A two step heat treatment would be necessary in this case.

In this article, steady state nucleation rates and transient times are calculated by CNT and by the Kashchiev [17] equation, respectively. Fortunately, recent computer simulations [18,19] demonstrated that excellent estimates for τ can be obtained by Kashchiev's expression. It should be stressed, however, that the predicted values for I (by CNT) will be many orders of magnitude lower than the

actual values [9,14] but the predicted temperature dependence will be good. Therefore, emphasis will be placed in the location of T_{\max} as well as on the magnitude of the induction periods.

The main objective of this paper is to demonstrate that the lack of observable homogeneous nucleation in glasses for which the predicted value of T_{\max} is low, i.e. $T_{\max} < T_g$, is due to slow molecular rearrangement and long induction periods to initiate nucleation below T_g .

THEORY

Steady State Nucleation

The Classical Nucleation Theory relates the steady-state nucleation frequency (I^0) to the thermodynamic (W^*) and kinetic (ΔG_D) molar free energy barriers by the expression:

$$I^0 = N^0 \nu \exp\left[-\frac{(\Delta G_D + W^*)}{RT}\right] \quad (1)$$

where N^0 is the total number of unit cells of the nucleating phase per unit volume of liquid, ν the vibration frequency, R is the gas constant and T the absolute temperature.

Assuming that the molecular rearrangement for crystal nucleation can be described by an effective diffusion coefficient, $D = \lambda^2 \nu \exp(-\Delta G_D/RT)$, and using the Stokes-Einstein expression, $D = kT/3\pi \eta a_0$, one has

$$I^0 = \frac{N^0 kT}{3\pi \eta a_0} \exp(-W^*/RT) \quad (2)$$

where a_0 has the magnitude of the molecular diameter and η is the viscosity coefficient. This equation has been shown to give a good description of the temperature dependence of the nucleation rates although the absolute values predicted for I^0 are many orders of magnitude smaller than the experimental values [9,14].

Transient Nucleation

The steady state nucleation rate in a supercooled liquid is not achieved immediately at a given temperature, but only after the elapse of a certain period of time required to create an equilibrium size distribution of crystalline embryos. A good analytical solution to the Zeldovich-Frenkel [20] equation has been proposed by Kashchiev [17]:

$$\tau = \frac{8 kT}{\nu^* \lambda^3 \rho^*} \quad (3)$$

where $\beta^* = - \left(\frac{\partial^2 \Delta G}{\partial n^2} \right)_{n^*}$, ΔG_n being the Gibbs free energy required to form a cluster of n formula units (n^* refers to the critical nucleus); S^* is the surface area of the critical nucleus and Γ is the number of formula units that join the critical nucleus per unit time per unit area and is given by

$$\Gamma = \frac{kT}{h\lambda^2} \exp\left(\frac{-\Delta G_D}{RT}\right) \quad (4)$$

James [21] rearranged Eqs. (3) and (4) to give:

$$\tau = \frac{16 h\lambda^2 \sigma}{\pi^2 \Delta G^2} \exp(\Delta G_D/RT) \quad (5)$$

where ΔG is the free energy difference between liquid and crystal. Assuming once more the Stokes-Einstein Equation:

$$\tau = \frac{48 \sigma \lambda^5 N_A^2}{\pi \Delta G^2} \eta \quad (6)$$

where N_A is Avogadro's number.

Experimental evidence for the non-steady state character of crystal nucleation in supercooled liquids was provided by Gutsow in 1966 [22]. Other studies were carried out by James in 1974 [21] and Kalinina, et. al. in 1977 [23]. For a good review on the subject the reader is referred to [22].

A specially important publication appeared in 1983 [18] based on a simulation of cluster populations and their evolution with time. An exact solution of the set of coupled differential equations, which describe the evolution of the cluster populations with time, was obtained and used to test a numerical simulation technique. The authors have shown that the "development" heat treatment, often used in nucleation experiments, leads to observed time lags greater, typically 2-5 times, than the real transient times at nucleation temperatures. The effective time lag in transient nucleation shows an Arrhenian behavior with an activation energy somewhat less than that for atomic mobility given as an input parameter. The presence of preexisting clusters, inherited from cooling down from higher temperatures, slightly shortens the effective time lag. The analysis of Kashchiev [17] was shown to yield a good experience for transient nucleation.

In a more recent publication Volterra and Cooper [19] carried out numerical simulations based on slightly different assumptions and, in agreement with [18], concluded that the Kashchiev solution is adequate for calculations of transient times at a fixed undercooling.

It should, therefore, be stressed that Kashchiev's Eq. (3) has been demons

trated to be correct and thus will be used to estimate the transient times in this article.

Calculations

Upper and lower bounds for the temperatures of maximum nucleation rates, transient times and critical nuclei radius can be obtained by using two different expressions for the thermodynamic driving force, ΔG , and by allowing the Turnbull ratio, α , to vary from 0,33 to 0,50 in Eqs. (2) and (6) to give:

$$I_{\ell}^{\circ} = \frac{N^{\circ} kT}{3\pi\lambda^3\eta} \exp\left(-\frac{16\pi \times 0.5^3 \times \Delta H_f T_f^2}{3RT (T_f - T)^2}\right) \quad (7)$$

$$I_{\mu}^{\circ} = \frac{N^{\circ} kT}{3\pi\lambda^3\eta} \exp\left(-\frac{4\pi \times 0.33^3 \times \Delta H_f T_f^2 (T_f + T)^2}{3RT^3 (T_f - T)^2}\right) \quad (8)$$

$$\tau_{\ell} = \frac{48 \times 0.33 \times \lambda^5 N_A^{5/3}}{\pi \Delta H_f v_m^{2/3}} \left\{ \frac{T_f}{(T_f - T)} \right\}^2 \eta \quad (9)$$

$$\tau_{\mu} = \frac{12 \times 0.50 \times \lambda^5 N_A^{5/3}}{\pi \Delta H_f v_m^{2/3}} \cdot \left\{ \frac{T_f (T_f + T)}{T (T_f - T)} \right\}^2 \eta \quad (10)$$

where $\lambda = 3\text{\AA}$, v_m is the molar volume, T_f is the melting temperature and ΔH_f is the molar heat of melting.

The critical nuclei radius, R^* , were calculated by

$$R^* = 2 \times 0.33 v_m^{1/3} T_f / (T_f - T) \quad (11)$$

and

$$R^* = 2 \times 0.50 v_m^{1/3} T_f (T_f + T) / (T (T_f - T)) \quad (12)$$

Therefore, in order to estimate the bounds for T_{\max} (from I° vs T curves), τ and R^* , the following parameters are necessary: the temperature dependence of viscosity (η), the melting enthalpy of the crystalline phase (ΔH_f) and the melting temperature (T_f).

RESULTS

Table I shows the thermodynamic and kinetic (viscosity) data used here. Table II shows both lower and upper bounds for T_{\max} and I_{\max} for 12 glass-forming systems. The glass transition region was taken as the temperature range where

Table I. Thermodynamic and kinetic (viscosity) data for several glass forming systems.

	Tf(K)	$\Delta H_f(\text{J/mol})$	A	B	To
NC ₂ S ₃	1564	87900	-4.86	4893	547
LS ₂	1307	57300	1.81	1347	595
BS ₂	1693	37000	1.83	1702	795
G	1387	15100	-9.94 -6.80	17962 16393	0 0
CAS ₂	1826	135500	-5.85	6750	738 -(1)
NS ₂	1147	35500 45190	-0.64	2315	541
LP	926	61700	-4.10	2000	462
P	853	21760 27200	-4.87	9071	0
PS	1037	34000 60420			-(2)
S	1996	15000	-13.51 -6.88	37157 27115	0 0
NAS ₆	1380	55000	-8.59	21338	0
B	723	22600	-5.02	3665	333

$\text{Log}(\eta) = A + B / (T - T_0)$, (Pa.s)

(1) $\text{Log}(\eta) = 12-54200/T + 61000000/T^2$

(2) $\text{Log}(\eta) = 10-28100/T + 19000000/T^2$

For simplicity the following notation is used:

1) NC₂S₃ = Na₂O.2CaO₂.3SiO₂; 2) LS₂ = Li₂O.2SiO₂; 3) BS₂ = BaO.2SiO₂

4) G = GeO₂; 5) CAS₂ = CaO.Al₂O₃.2SiO₂; 6) NS₂O.2SiO₂;

7) LP = Li₂O.P₂O₅; 8) P = P₂O₅; 9) PS = PbO.SiO₂; 10) S = SiO₂;

11) NAS₆ = Na₂O.Al₂O₃.6SiO₂; 12) B = B₂O₃

Table II. Results for temperature (T_{\max}) and magnitude of maximum nucleation rates (I_{\max})

	From Equation 7			From Equation 8	
	T_g/T_f	T_{\max}/T_f	$\text{Log}(I_{\max})^*$	T_{\max}/T_f	$\text{Log}(I_{\max})$
NC_2S_3	.53-.55	.52	-28	.61	-3
LS_2	.56-.57	.55	-19	.61	+3
BS_2	.57-.58	.59	+ 3	.65	+16
G	.59-.62 .63-.66	.59 .58	+13 +12	.70 .69	+20 +19
CAS_2	.61-.62 .62-.63	.55 .52	-55 -54	.62 .62	-18 -19
NS_2	.63-.65	.60 .59	-13 -22	.66 .66	+7 +2
P	.63-.67	.50 .48	-2 -8	.63 .61	+9 +5
LP	.63-.64	.59	-56	.65	-16
PS	.65-.67	.58 .54	-17 -42	.67 .64	+4 -12
S	.72-.76 .73-.76	.63 .65	+13 +12	.73 .75	+10 +10
NAS_6	.75-.79	.49	-20	.62	-3
B	.76-.78	.64	-28	.70	-2

* I_{\max} ($\text{m}^{-3} \cdot \text{s}^{-1}$)

$$10^{11} < \eta < 10^{12} \text{ Pa.s.}$$

Figure 1 shows the reduced temperatures of maximum nucleation as a function of the reduced glass transition temperature (range). The geometrical figures represent the most probable location for the calculated upper and lower limits of T_{\max}/T_f . The use of viscosity and heats of melting from different sources, available in the literature for some systems, has led to the areas of highest probability (geometrical figures). When single values of ΔH_f and Fulcher parameters were employed, horizontal lines resulted for both upper and lower T_{\max} .

The experimental points for glasses which nucleate homogeneously (NC_2S_3 , LS_2 , BS_2) are close to the lower calculated bounds for T_{\max} . Other general observations can be made: First, all oxide glasses which show copious homogeneous nucleation have low values of T_g/T_f (0.58 or less), as pointed out by James [24], and both predicted and experimental T_{\max} lie close to or above T_g . In the intermediate region ($0.59 < T_g/T_f < 0.67$) the upper limits lie at or above T_g and vice versa. Glasses G, CAS_2 , P, LP and NS_2 belong to this region. Third, for glasses with high T_g , $T_g/T_f > 0.72$ (PS, S, NAS_6 and B), both limits of T_{\max} are below T_g and reportedly these glasses nucleate heterogeneously. This figure is an expanded, improved version of Fig. 3 in reference [14] and allowed the determination of the intermediate region for T_g/T_f , although the main features presented in [14] are still preserved.

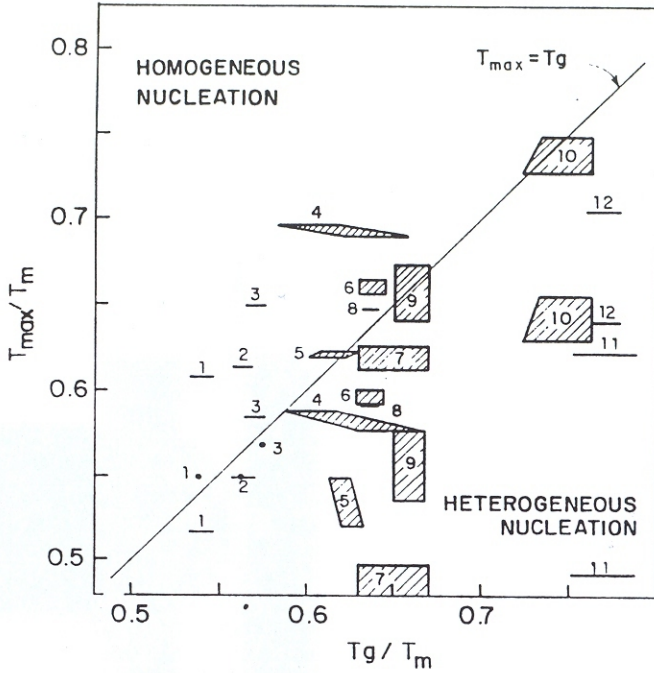


Fig. 1. Upper and lower bounds for calculated values of reduced temperature of lower maximum nucleation frequency, T_{\max}/T_f versus reduced glass transition temperature interval T_g/T_f (lines and geometrical figures).

Figure 2 compares experimental and calculated induction periods for LS_2 and NC_2S_3 glasses. The calculated curves were obtained through Eqs. (9) and (10) and are close to the experimental points. The temperature dependence, however, are different and lead to overestimates below T_g and vice versa. The agreement at T_g is excellent for LS_2 .

Figure 3 shows the calculated values of $\log(\tau)$ as a function of T_f/T (inverted reduced temperatures), in the temperature range where homogeneous nucleation is expected to occur, i.e. between the calculated limits of T_{max}^{***} . The values of T_g/T_f increase in order 1 to 12 and clearly show that glasses 1 to 3 ($T_g/T_f < 0.58$) have short transient times. For systems 4 to 8 ($0.59 < T_g/T_f < 0.67$) the induction periods vary from minutes to several days, the exception being GeO_2 which show short induction times in the whole nucleation range. Glasses 9 to 12 ($T_g/T_f > 0.72$) have exceptionally long transient times, approaching millions of years for albite (NAS_6) and B_2O_3 .

DISCUSSION

James [24] has demonstrated that for seven homogeneously nucleating glasses the experimental values of T_{max} are always at or somewhat above T_g and T_g/T_f is in the range 0.54 to 0.59. In a previous publication [14], this author has shown that the calculated values of T_{max} are also at or above T_g for homogeneous nucleation, in agreement with James. Additionally, it was demonstrated that the reverse also applies, i.e. if $T_{max} < T_g$ only surface (heterogeneous) nucleation is observed. This was postulated to be due to long induction times for homogeneous nucleation below T_g , although no quantitative evidence for τ was provided.

The objectives of this paper are twofold: to calculate the magnitude of transient times in the temperature range where nucleation is likely to occur (between the limits for T_{max}); and to test the sensitivity of T_{max} by varying the input parameters in Equations (6) and (7).

Figure 1 is an improved version of Fig. 3 in the previous paper [14] with some additional features. The Turnbull ratio varied from 0.33 to 0.50, a wider and more correct range than previously used (0.42 - 0.55). This shifted both upper and lower T_{max} to higher temperatures. The use of several combinations of viscosity and/or heats of fusion for some systems yielded probability regions for the limits of T_{max} instead of the localized points obtained in [14]. Furthermore, the calculations for albite (NAS_6) and P_2O_5 are presented for the first time.

***In actual fact, nucleation can be appreciable in a narrow range ($\pm 30^\circ C$) above and below T_{max} .

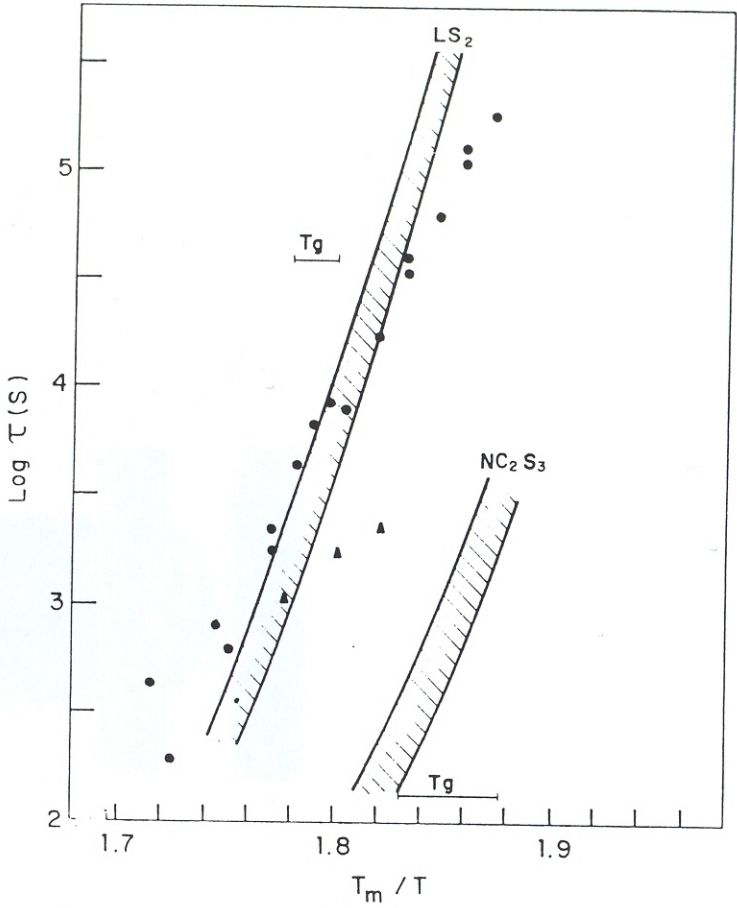


Fig. 2. Calculated (▨) and experimental (\bullet , \blacktriangle) transient times for LS_2 and NC_2S_3 as a function of inverted reduced temperatures. Data points from [21,23].

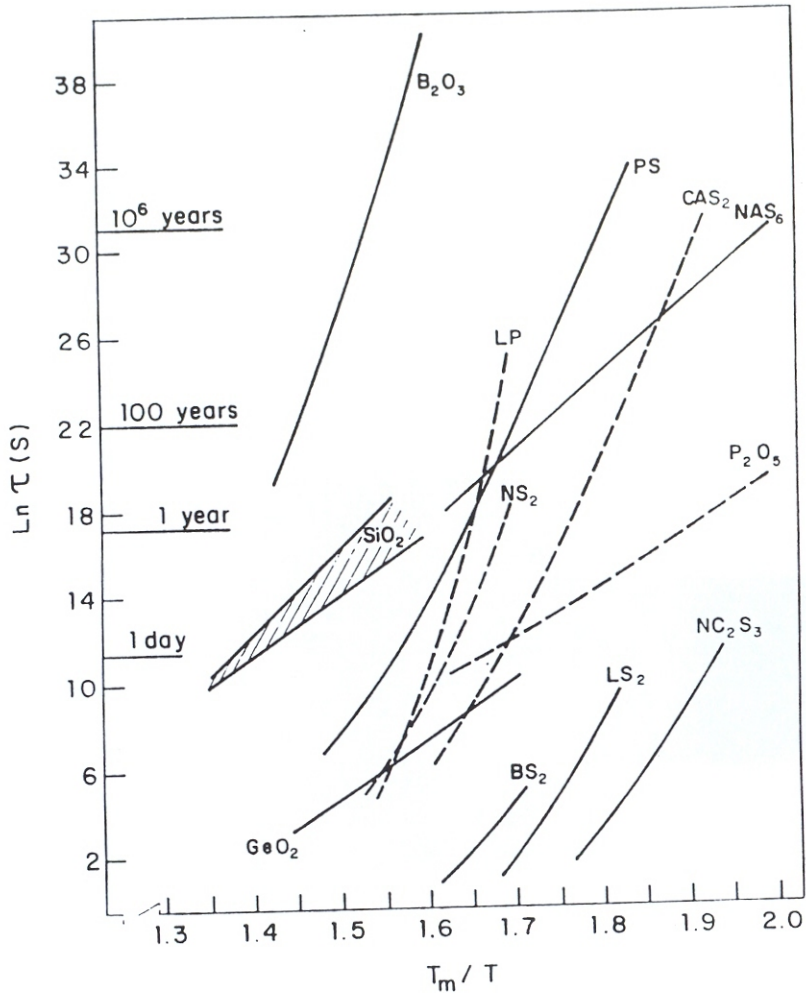


Fig. 3 Calculated values of transient times in the nucleation range, defined here as ΔT_{max} .

The general observations of [14] are confirmed and additional, more subtle points are revealed: i) for low values of T_g , $T_{max} > T_g$ and homogeneous nucleation is experimentally detected; ii) for high values of T_g , $T_{max} < T_g$ and only surface (heterogeneous) nucleation is observed; iii) for intermediate values of ($0.59 < T_g/T_f < 0.67$) the upper limits of T_{max} lie close to or at just above T_g while the lower bounds lie below T_g . The exception is GeO_2 for which the upper bounds are well above T_g .

In these latter systems only anorthite has been reported to show internal nucleation [25]; however, this system presents several unusual features: i) Anorthite glass has a very small nucleation rate ($I_{max} = .004mm^{-3} s^{-1}$), several orders of magnitude smaller than that of other glasses such as LS_2 , BS_2 , NC_2S_3 . The experimental ratio T_{max}/T_f is 0.68 which is much higher than T_g/T_f (0.62) and than the calculated upper limit ($T_{max}/T_g = 0.62$). Therefore, this glass seems to be the sole exception among the 12 systems studied and deserves further attention, although this will not be covered in this paper. However, homogeneous nucleation cannot be ruled out for this family of glasses since the upper limits for T_{max} are at or above T_g .

The calculations also indicate that T_{max} increases for increasing values of activation energy for viscous flow and for decreasing values of surface energy, α , and of heat of fusion, ΔH_f . This was verified for those systems where different data sets are available. These observations are in agreement with Weinberg's predictions [26].

Table II shows that there is no obvious trend for the magnitude of I_{max} with T_g . In general, $-56 < \log(I_{max}) < +16$ ($m^{-3} \cdot s^{-1}$) within the three groups of glasses. It should be emphasized, however, that the predicted magnitudes of I_{max} for LS_2 , BS_2 and NC_2S_3 are many orders of magnitude lower than the experimental values, and thus CNT underestimates I_{max} .

As the minimum detectable rate is close to $10^3 m^{-3} \cdot s^{-1}$ it is reasonable to expect that those systems for which the calculated values of I_{max} are large, $\log(I_{max}) > 3$, will present measurable homogeneous nucleation unless the transient times are excessively long at temperatures close to T_{max} . It is interesting to point out that the predicted steady state nucleation rates are highest for SiO_2 and GeO_2 ($12 < \log(I_{max}) < 20$) and compares to the highest homogeneous crystal nucleation frequency ever reported for oxide glasses, i.e. $10^{14} m^{-3} s^{-1}$ for N_2CS_3 [27].

Table III shows the calculated critical nuclei radius, $R^*(T_{max})$, for the 12 glasses studied. It varies from 10 to 16 Å, as predicted by Weinberg and Neilson [28] for oxide glasses. It is illustrative, however, to estimate the number of unit cells (n^*) necessary to build the critical nucleus. Table III shows that n^* varies from 6 to 60 unit cells, which are reasonable values and indicate that the approximations used here are adequate.

TABLE III. Critical nuclei size (n^*) for several oxide glasses.

System	R*(Å)	Crystal Type	$v^0 (10^{30} \text{ m}^3)$	n^*
NC_2S_3	12-13			
LS_2	10	Ort	408.6	11
BS_2	12			
G	9-10	l-Tet h-Hex	55.3 121.7	62 28
CAS_2	12	Tri Hex ort	1339.0 332.0 341.4	6 24 23
NS_2	12			
P				
LP	9			
PS	10			
S	11-12	C-Tet C-Cub	171.0 363.7	37 17
NAS_6	14-16	l-Tri h-Tri	664.6 667.0	21 21
B	10	Hex	135.1	29

Since the standard double stage heat treatment have been used to obtain the experimental transient times τ_{ex} , in [21, 23 and 25], it should be stressed that τ_{ex} is a sum of the real induction period, τ , and the time required to grow the critical nuclei from the nucleation to the development temperature size. Therefore, the experimental values indicated in Figures 2 and 3 overestimates by 2 to 5 times the actual τ [18]. On the other hand, the use of extrapolated data from the supercooled liquid values (by means of Fulcher equation) leads to "equilibrium" viscosity values below T_g , which overestimates the calculated τ . Thus the comparison of experimental and calculated transient times in Figure 2 directs attention to the upper limits. Figure 2 also demonstrates that the use of different thermodynamic and kinetic (viscosity) data does not affect significantly the predicted values of induction times.

The activation energies for induction, given by the slopes in Fig: 2, however, are constant, and clearly different from that for viscous flow which increase with increasing temperatures in the nucleation range. This observation has an important bearing in relation to the physics of the nucleation process

since the molecular rearrangements for nucleation should, in principle, be equivalent to those for induction periods. This was discussed in a previous paper [29].

Taken in toto, the results of Figure 2 demonstrate that the use of Kashchiv's equation, viscosity and thermodynamic data, assuming the Stokes-Einstein expression, give reasonable estimates for τ at the glass transition interval, i.e. within three orders of magnitude in the temperature range of observable transient times.

The interesting (and intriguing) observation that both the experimental and calculated values to T_{\max} always lie close to T_g for homogeneous nucleation can now be understood.

A sizeable undercooling, $1 - T_{\max}/T_f = 0.20 - 0.67$, is necessary to induce appreciable homogeneous nucleation [26] and thus one expects this to be of the same order or larger than $1 - T_g/T_f$, since this latter quantity varies from 0.2 to 0.5 for laboratory (time scales) experiments. Indeed, larger supercoolings (> 0.5) or $T_{\max} < T_g$ would be even more favorable for nucleation from a purely thermodynamic point of view, since the kinetic contribution is approximately equal for all glasses at the transition range ($\eta \approx 10^{12}$ Pa.s).

The well known fact that the large majority of glasses nucleate from the surfaces and only a few glass systems show homogeneous nucleation supports the assumption that there is a need for high undercoolings ($T_{\max} < T_g$) for internal nucleation. For these latter systems, however, the induction times are excessively long and homogeneous nucleation cannot be observed in reasonable times. Hence, for glasses where homogeneous nucleation can be detected one expects that $T_{\max} > T_g$.

It should be stressed, however, that the actual location of T_{\max} depends upon the values of several parameters; T_{\max} will be higher for high values of the activation energy for viscous flow and of the ratio $\Delta C_p \cdot T_f / \Delta H_f$ [26], where ΔC_p is the difference in specific heat between the crystal and liquid. Low values of interfacial energy (or α) will also lead to high T_{\max} and thus favor homogeneous nucleation.

For the purpose of this article, Fig. 3 is the most enlightening especially when viewed in conjunction with Fig.1. It clearly shows that within the nucleation temperature range, the predicted induction periods increase with reduced glass transition temperature. For instance, $\tau < 1$ day for NC_2S_3 ($T_g/T_f=0.54$) and $\tau > \text{year}$ for B_2O_3 ($T_g/T_f=0.77$). This might explain the lack of observable homogeneous nucleation in glasses with high values of T_g/T_f and vice versa. Another possibility is that the magnitudes of the steady state nucleation rates are too low in the range where the induction times are small i.e. for $T > T_{\max}$. Unfortunately this possibility cannot be tested at the present time due to the inability of CNT to make quantitative predictions.

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REFERENCES

1. E.D. Zanotto and A.F. Craievich, J. Mat. Science 16 (1981) 973.
2. E.D. Zanotto, A.H. Ramsdem, A.F. Craievich and P.F. James, Proc. Symposium on Phase Transformations in Vitreous Systems, Warwick (1981).
3. E.D. Zanotto, A.F. Craievich and P.F. James - Journal de Physique 43, (1982) 107.
4. S. Bras, A.F. Craievich, J.M. Sanches, C. Williams and E.D. Zanotto, Nuclear Instruments and Methods, 208 (1983) 489.
5. E.D. Zanotto, J. Amer. Ceram. Soc., 66 (1983) C-37.
6. A.F. Craievich, E.D. Zanotto and P.F. James, Bull. Soc.Min. et. Cryst. 106 (1983) 169.
7. E.D. Zanotto and P.F. James, Glastech. Ber. 56K (1983) 794 (XIII International Glas Kongress, July 1983, Hamburg).
8. E.D. Zanotto, P.F. James and A.F. Craievich, J. Mat. Science 21 (1986) 3050.
9. E.D. Zanotto and P.F. James, J. Non-Cryst. Solids 74 (1985) 373.
10. E.D. Zanotto and A.C. Galhardi, Proc. 6ª CBECIMAT, Rio de Janeiro-RJ (1984) 30.
11. E.D. Zanotto and A.C. Gualhardi, J. Non-Cryst. Solids 104 (1988) 73.
12. E.D. Zanotto and P.F. James, J. Non-Cryst. Solids 104 (1988) 70.
13. E.D. Zanotto and R. Basso, Cerâmica 32 (1986) 117.
14. E.D. Zanotto, J. Non-Cryst. Solids 89 (1981) 361.
15. E. Meyer, J. Cryst. Growth 74 (1986) 425.
16. E. Meyer, J. Cryst. Growth 84 (1987) 533.
17. D. Kashchiev, Surf. Science 14 (1969) 209.
18. K.F. Kelton, A.L. Greer and C.V. Thompson, J. Chem. Phys. 79 (1983) 6261.
19. V. Volterra and A.R. Cooper, J. Non-Cryst. Solids 74 (1985) 85.
20. J.B. Zeldovich, Acta Physics Chim. URSS 18 (1943) 1.
21. P.F. James, Phys. Chem. Glasses 15 (1974) 95.
22. I. Gutsow, Contemp. Phys. 21 (1980) 121; 21 243.
23. A.M. Kalinina, V.M. Fokin and V.N. Filipovich, Fiz. Khim. Stekla 2 (1977) 122
24. P.F. James, J. Non-Cryst. Solids 73 (1985) 517.
25. A. Hishinuma and D.R. Uhlmann, J. Non-Cryst. Solids 95 & 96 (1987) 449.
26. M.C. Weinberg, J. Non-Cryst. Solids 83 (1986) 9d.
27. A.M. Kalinina, V.N. Filipovich and V.M. Fokin, J. Non-Cryst. Solids 38 & 39 (1980) 723.
28. M.C. Weinberg and G.F. Neilson, J. Non-Cryst. Solids 74 (1985) 177.
29. M.C. Weinberg and E.D. Zanotto. J. Non-Cryst. Solids 108 (1989) 99.