

Trends in homogeneous crystal nucleation in oxide glasses

E. D. Zanotto* & M. C. Weinberg

Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85712, USA

Manuscript received 26 September 1988

Calculations are performed to estimate the temperature of maximum nucleation rate, T_{max} , for several oxide glasses. It is found that for one class of glasses for which $T_{max} \ll T_g$ (where T_g is the glass transition temperature), homogeneous crystal nucleation has never been experimentally observed. The postulate that the failure to detect homogeneous nucleation in these glasses is due to transient nucleation effects is tested for several cases. It is concluded that for some glasses, such as B_2O_3 and $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ (albite), long transient times appear to be a contributing factor to the prevention of homogeneous crystallisation. However, it is demonstrated that transient nucleation effects are not responsible for the fact that homogeneous nucleation would not be observed in $Na_2O \cdot 2SiO_2$ and $PbO \cdot SiO_2$. Hence, the failure of glasses with low T_{max} to crystallise homogeneously cannot in general be attributed to transient effects and one must conclude that their steady state nucleation rates are particularly small.

Although a large amount of information exists regarding crystal nucleation in glasses, during the past 10–15 years the realisation has developed that several basic questions pertaining to nucleation in glasses remain unresolved.^(1–4) This has come about, in part, due to a number of experimental studies in which homogeneous crystal nucleation rates in simple glass compositions have been measured.^(5–8) Hence there has been an effort to obtain homogeneous crystal nucleation data in as many systems as possible.

During the course of this endeavour two difficulties have been encountered. First, homogeneous and heterogeneous nucleation are not always unambiguously distinguishable, and this problem has been addressed in several works;^(9–11) second, a very limited number of simple glass compositions appear to exhibit homogeneous crystal nucleation. Although an explanation can be given for this with some systems, in general this finding is not understood. Homogeneous nucleation seems to appear at rather large undercoolings while certain compositions show a tendency towards surface nucleation at relatively small undercoolings and if the

surface nucleated crystallites also tend to exhibit rapid growth, then complete crystallisation of the sample may ensue at modest undercoolings. Under such circumstances deep undercooling of the glass is prevented, and hence it would be impossible to seek homogeneous crystal nucleation in such systems.

For a number of glass compositions, however, deep undercoolings are possible with a minimal (or at least tolerable) amount of surface crystallisation in evidence. Under these circumstances it is feasible to seek for signs of homogeneous nucleation; a number of such experiments have been performed, and homogeneous nucleation has been detected in only a small percentage of the systems studied.

Three conditions must be satisfied for homogeneous crystal nucleation to be observable (by common microscopic techniques): (i) the crystal growth rate must be sufficiently large (in some temperature region) so that the nuclei can be grown to a size where they are detectable; (ii) the steady state homogeneous nucleation rate must be sufficiently large (say greater than $10^3 \text{ m}^{-3} \text{ s}^{-1}$) in order to form a sufficient number of particles within a reasonable time; (iii) the transient times cannot be too long in the temperature region of significant nucleation. In most cases condition (i) is easily satisfied but there are a few notable exceptions, two of which will be mentioned herein. Hence, the detection of homogeneous nucleation usually depends upon the magnitude of the steady state rate or the length of transient times in the nucleation region.

In the present work we observe a trend in the experimental results gathered to date. Homogeneous nucleation has been reported for glass compositions which have relatively low reduced glass transition temperatures, T_g/T_m , and whose (predicted and observed) temperature at which maximum nucleation occurs, T_{max} , lies above the glass transition temperature. On the other hand, homogeneous nucleation has not been reported (at least for inorganic glasses) for those compositions for which the temperature of maximum (predicted) homogeneous nucleation occurs below the glass transition temperature. It might be suspected that the latter compositions have long transient times and hence that the lack of observable homogeneous

*On sabbatical leave from Universidade Federal de Sao Carlos, Brazil.

nucleation in such systems is due to transient effects; this hypothesis is analysed in detail for several compositions.

Trends in the location of the nucleation curve

For seven glass compositions James⁽¹⁾ demonstrated that the experimental values of T_{\max} are always at or somewhat above T_g and that T_g/T_m is in the range 0.54 to 0.59. In a recent publication^(1,2) one of the present authors shows that, for homogeneous nucleation, the calculated values of T_{\max} are also close to T_g , in agreement with James's observations; it was also demonstrated that the reverse also applies, i.e. if the predicted T_{\max} falls below T_g , only surface (heterogeneous) nucleation is observed.

Here, we calculate T_{\max} for 12 oxide glasses. It should be emphasised, however, that the values for I° predicted by classical nucleation theory are many orders of magnitude lower than the actual values⁽¹⁻⁷⁾ but the predicted temperature dependence is well described by theory when the viscosity is used to estimate the kinetic barrier. Therefore, only the location of T_{\max} will be computed.

Location of the steady state maximum nucleation rate

The steady state nucleation rate, according to classical theory, may be written⁽¹⁾

$$I^\circ = \frac{CT}{\eta(T)} \exp(-W^*/RT) \quad (1)$$

where C is a constant, T is temperature, η is the viscosity, R is the gas constant, and W^* is the bulk free energy required to form a critical nucleus which, for spherical nuclei, is given by

$$W^* = \frac{16\pi\sigma^3}{3(\Delta G_v)^2} \quad (2)$$

where σ denotes the liquid-crystal surface energy and ΔG_v is the bulk free energy difference between liquid and crystal per unit volume.

The temperature at which the nucleation rate is maximum can be obtained by solving the equation $dI^\circ/dT=0$. If a reduced temperature, T_r , is defined as T/T_m , where T_m is the melting temperature, and β is the entropy of fusion in units of R , then the temperature of maximum steady state nucleation rate may be found from

$$T_r + \frac{b}{(1 - T_{or}/T_r)^2} + \frac{16\pi\alpha^3\beta}{3} j(T_r; \gamma) h(T_r; \gamma) = 0 \quad (3)$$

where

$$j \equiv \frac{1 - 2T_r(1 + \gamma \ln T_r)}{\Delta T_r(1 - \gamma) - \gamma T_r \ln T_r} \quad (4)$$

$$h \equiv [\Delta T_r(1 - \gamma) - \gamma T_r \ln T_r]^{-2}. \quad (5)$$

In deriving Equation (3), it has been assumed that the difference in specific heat between crystal and liquid, ΔC_p , is constant and $\gamma = \Delta C_p/\Delta S_m$ (where ΔS_m is the

entropy of fusion); furthermore, it was assumed that σ is proportional to the enthalpy of fusion with α , the Turnbull ratio, ranging from 1/3 to 1/2; finally, $\Delta T_r = 1 - T_r$. The viscosity was taken to be of the Fulcher form,

$$\ln \eta = a + \frac{b}{T_r - T_{or}}. \quad (6)$$

Table 1 shows the thermodynamic and viscosity data employed in the present calculations and the results are shown in Figure 1, where the reduced maximum nucleation temperatures are plotted against T_g/T_m ; the predictions are given as lines or geometrical figures rather than points. The extension along the

Table 1. Thermodynamic and viscosity data for several glass forming systems

Glass	T_m (K)	ΔH_m (J/mole)	A	B	T_0
1. Na ₂ O.2CaO.3SiO ₂	NC ₂ S ₃ 1564	87900	-4.86	4893	547
2. Li ₂ O.2SiO ₂	LS ₂ 1307	57300	1.81	1347	595
3. BaO.2SiO ₂	BS ₂ 1693	37000	1.83	1702	795
4. GeO ₂	G 1387	15100	-9.94	17962	0
			-6.80	16393	0
5. CaO.Al ₂ O ₃ .2SiO ₂	CAS ₂ 1826	135500	-5.85	6750	738
			-0.64	2315	541
6. Na ₂ O.2SiO ₂	NS ₂ 1147	35500			
		45190			
7. Li ₂ O.P ₂ O ₅	LP 926	61700	-4.10	2000	462
8. P ₂ O ₅	P 853	21760	-4.87	9071	0
		27200			
9. PbO.SiO ₂	PS 1037	34000			
		60420			
10. SiO ₂	S 1996	15000	-13.51	37157	0
			-6.88	27115	0
11. Na ₂ O.Al ₂ O ₃ .6SiO ₂	NAS ₆ 1380	55000	-8.59	21338	0
12. B ₂ O ₃	B 723	22600	-5.02	3665	333

$$\log(\eta) = A + B/(T - T_0) \text{ Pa s} \quad (1) \log(\eta) = 12 - 54200/T + 61000000/T^2$$

$$(2) \log(\eta) = 10 - 28100/T + 19000000/T^2$$

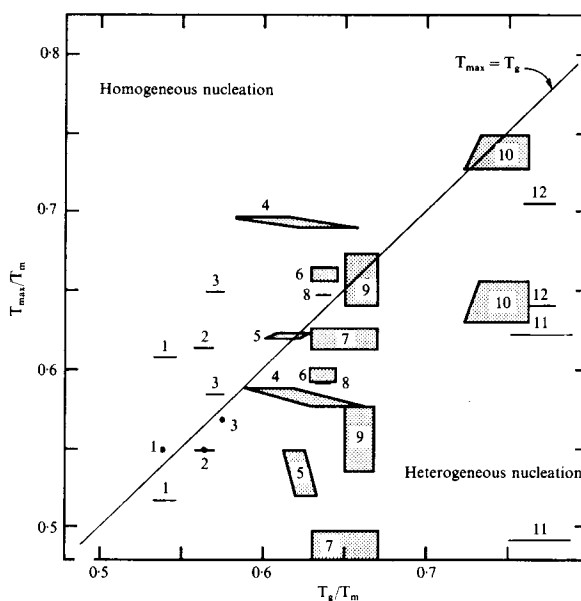


Figure 1. Plot of the calculated values of reduced temperature of maximum nucleation frequency against reduced glass transition temperature interval (lines and geometrical figures)

● experimental points for NC₂S₃, LS₂, and BS₂ glasses

abscissa corresponds to the temperature region of the glass transition while the breadth in the direction of the ordinate is caused by differences in the viscosities and heats of fusion found by different investigators. One should note that two lines (or figures) are given for each material; these correspond to upper and lower bounds for T_{\max}/T_m and respectively correspond to the most common choices of 1/3 and 1/2 for the Turnbull ratio and to variations of γ from 0 to a positive value < 2.0.

For systems in which homogeneous nucleation has been observed, the predicted values of T_{\max} typically lie at or about T_g . The points in Figure 1 represent values of T_{\max}/T_m determined experimentally for the three systems for which $T_{\max} \approx T_g$. For those systems in which homogeneous nucleation could not be detected (e.g. PS, S, B, and NAS_6), the predicted values of T_{\max} fall below T_g . Figure 1 is an expanded, improved version of Figure 3 in Reference 12, but the main features are preserved.

Transient nucleation

The nucleation rate in a supercooled liquid is time dependent until the time required to create a steady state size distribution of crystalline embryos has elapsed; this initial period is termed transient nucleation. Experimental evidence for the non steady state character of crystal nucleation in supercooled liquids was provided by Gutzow in 1966⁽¹³⁾ and additional studies of transient nucleation were carried out by James⁽⁸⁾ and Kalinina *et al.*⁽¹⁴⁾

Recently, an exact solution of the set of coupled differential equations which govern the time evolution of the cluster populations was obtained analytically via numerical simulation.⁽¹⁵⁾ It was shown that the 'development' heat treatment often used in nucleation experiments leads to observed time lags typically 2–5 times greater than the real transient times at nucleation temperatures. The effective time lag in transient nucleation shows an Arrhenian behaviour, with an activation energy somewhat less than that for atomic mobility. The presence of preexisting clusters, inherited from cooling from higher temperatures, slightly shortens the effective time lag. Finally, it was demonstrated that the simple results of the approximate analysis of Kashchiev⁽¹⁶⁾ give a very good approximate description of transient nucleation.

In a more recent publication, Volterra & Cooper⁽¹⁷⁾ carried out numerical simulations based on slightly different assumptions and in agreement with Kelton *et al.*⁽¹⁵⁾ concluded that the Kashchiev solution is adequate for calculations of transient times at a fixed undercooling. Since Kashchiev's results are accurate and simple, they will be used to estimate the transient times in this article.

Kashchiev proposed an approximate analytical solution to the Zeldovich–Frenkel⁽¹⁸⁾ equation, with the transient time given by

$$\tau = \frac{8kT}{\pi^2 S^* \beta^* \Gamma} \quad (7)$$

where $\beta^* = -(\partial^2 \Delta G_n / \partial n^2)_{n^*}$ (in which ΔG_n is the Gibbs free energy required to form a cluster of n formula units and 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 given by

$$\Gamma = \frac{kT}{h\lambda^2} \exp\left(\frac{-\Delta G_D}{RT}\right) \quad (8)$$

James⁽¹⁾ rearranged Equations (7) and (8) and used the Stokes–Einstein equation to give

$$\tau = \frac{48\lambda^5 N_A^2 \sigma}{\pi \Delta G^2} \quad (9)$$

where N_A is Avogadro's number and λ is the jump distance.

Figure 2 compares experimental and calculated (Equation (9)) induction periods for LS_2 and NC_2S_3 glasses, and it may be seen that the calculated curves are close to the experimental points. However, the temperature dependences differ somewhat and lead to overestimates of τ below T_g and vice versa; the agreement at T_g is excellent for LS_2 . Also, experimental and predicted values of transient times for anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) glass are in fairly good agreement and, as observed for the other two systems, the data points for temperatures above T_g are somewhat higher than the predicted values.

The results of Figure 2 demonstrate that the use of Equation (9) gives good predictions for τ in the glass transition interval and overestimates τ when $T < T_g$. Overall, the experimental and calculated values of the relaxation times are within 2 or 3 orders of magnitude of each other.

Figure 3 shows the calculated values of τ in the temperature range where the steady state nucleation

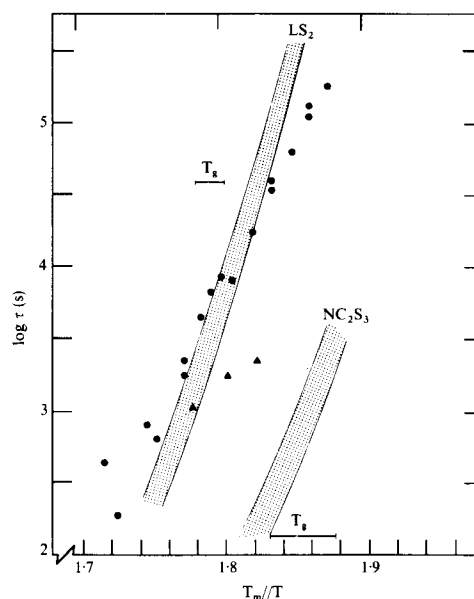


Figure 2. Calculated (dotted areas) and experimental transient times for LS_2 (●) and NC_2S_3 (▲) as a function of inverted reduced temperatures. Data points from References 8, 14, and 19

abscissa corresponds to the temperature region of the glass transition while the breadth in the direction of the ordinate is caused by differences in the viscosities and heats of fusion found by different investigators. One should note that two lines (or figures) are given for each material; these correspond to upper and lower bounds for T_{\max}/T_m and respectively correspond to the most common choices of 1/3 and 1/2 for the Turnbull ratio and to variations of γ from 0 to a positive value < 2.0 .

For systems in which homogeneous nucleation has been observed, the predicted values of T_{\max} typically lie at or about T_g . The points in Figure 1 represent values of T_{\max}/T_m determined experimentally for the three systems for which $T_{\max} \approx T_g$. For those systems in which homogeneous nucleation could not be detected (e.g. PS, S, B, and NAS_6), the predicted values of T_{\max} fall below T_g . Figure 1 is an expanded, improved version of Figure 3 in Reference 12, but the main features are preserved.

Transient nucleation

The nucleation rate in a supercooled liquid is time dependent until the time required to create a steady state size distribution of crystalline embryos has elapsed; this initial period is termed transient nucleation. Experimental evidence for the non steady state character of crystal nucleation in supercooled liquids was provided by Gutzow in 1966⁽¹³⁾ and additional studies of transient nucleation were carried out by James⁽⁸⁾ and Kalinina *et al.*⁽¹⁴⁾

Recently, an exact solution of the set of coupled differential equations which govern the time evolution of the cluster populations was obtained analytically via numerical simulation.⁽¹⁵⁾ It was shown that the 'development' heat treatment often used in nucleation experiments leads to observed time lags typically 2–5 times greater than the real transient times at nucleation temperatures. The effective time lag in transient nucleation shows an Arrhenian behaviour, with an activation energy somewhat less than that for atomic mobility. The presence of preexisting clusters, inherited from cooling from higher temperatures, slightly shortens the effective time lag. Finally, it was demonstrated that the simple results of the approximate analysis of Kashchiev⁽¹⁶⁾ give a very good approximate description of transient nucleation.

In a more recent publication, Volterra & Cooper⁽¹⁷⁾ carried out numerical simulations based on slightly different assumptions and in agreement with Kelton *et al.*⁽¹⁵⁾ concluded that the Kashchiev solution is adequate for calculations of transient times at a fixed undercooling. Since Kashchiev's results are accurate and simple, they will be used to estimate the transient times in this article.

Kashchiev proposed an approximate analytical solution to the Zeldovich–Frenkel⁽¹⁸⁾ equation, with the transient time given by

$$\tau = \frac{8kT}{\pi^2 S^* \beta^* \Gamma} \quad (7)$$

where $\beta^* = -(\partial^2 \Delta G_n / \partial n^2)_{n^*}$ (in which ΔG_n is the Gibbs free energy required to form a cluster of n formula units and 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 given by

$$\Gamma = \frac{kT}{h\lambda^2} \exp\left(\frac{-\Delta G_D}{RT}\right) \quad (8)$$

James⁽¹⁾ rearranged Equations (7) and (8) and used the Stokes–Einstein equation to give

$$\tau = \frac{48\lambda^5 N_A^2 \sigma}{\pi \Delta G^2} \eta \quad (9)$$

where N_A is Avogadro's number and λ is the jump distance.

Figure 2 compares experimental and calculated (Equation (9)) induction periods for LS_2 and NC_2S_3 glasses, and it may be seen that the calculated curves are close to the experimental points. However, the temperature dependences differ somewhat and lead to overestimates of τ below T_g and vice versa; the agreement at T_g is excellent for LS_2 . Also, experimental and predicted values of transient times for anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) glass are in fairly good agreement and, as observed for the other two systems, the data points for temperatures above T_g are somewhat higher than the predicted values.

The results of Figure 2 demonstrate that the use of Equation (9) gives good predictions for τ in the glass transition interval and overestimates τ when $T < T_g$. Overall, the experimental and calculated values of the relaxation times are within 2 or 3 orders of magnitude of each other.

Figure 3 shows the calculated values of τ in the temperature range where the steady state nucleation

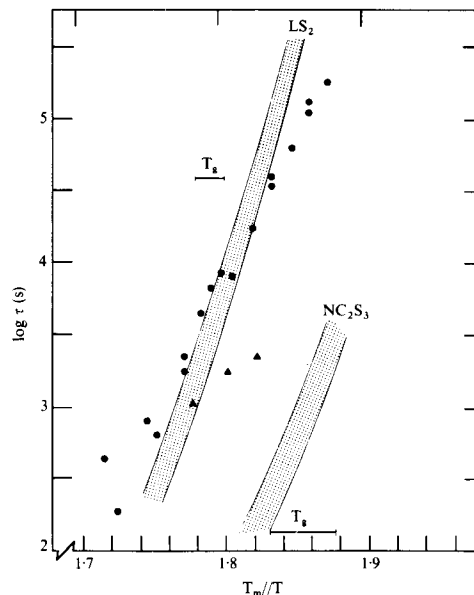


Figure 2. Calculated (dotted areas) and experimental transient times for LS_2 (●) and NC_2S_3 (▲) as a function of inverted reduced temperatures. Data points from References 8, 14, and 19

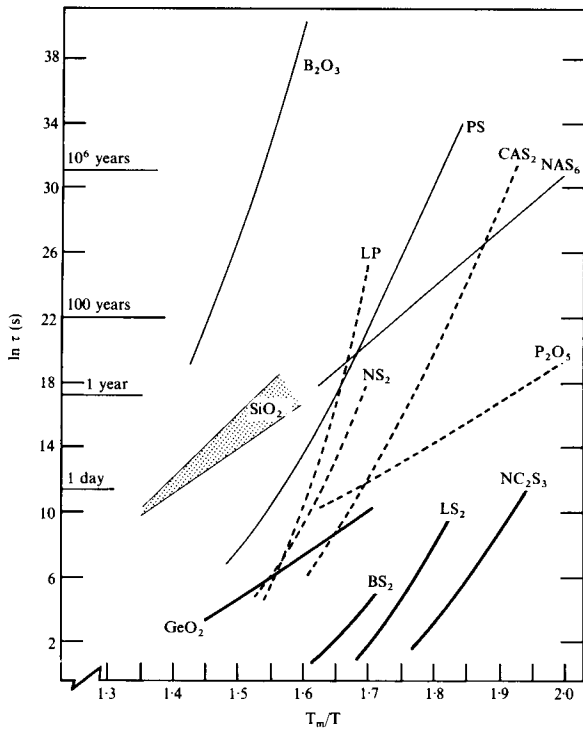


Figure 3. Predicted values of transient times in the temperature range where the nucleation rates should be highest, i.e. between the two limits of T_{max}

rates are expected to be maximum, i.e. between the two limits for T_{max} . The induction periods increase with increasing T_{gr} (reduced glass transition temperature), being quite short for glasses with low T_{gr} and extremely long for compositions with $T_{gr} > 0.75$. Hence, one might conclude that the fact that homogeneous crystal nucleation could not be observed in these systems is due to the suppression of the actual nucleation rate in comparison to the steady state rate. This point is illustrated in Table 2 where the transient times at the temperature of maximum nucleation and the ratio of actual to steady state nucleation rates are listed for those systems possessing very long transient times: it may be observed that the nucleation rates are very small fractions of the steady states rates even after prolonged heating. These data seem to support the hypothesis that the absence of homogeneous nucleation results from transient effects and in the remainder of this work the plausibility of this argument is analysed in more detail and comparisons are made with experimental findings.

Table 2. Predicted values for $\alpha = 1/2$

System	T_{max}	$\tau(T_{max})$ (s)	I/I^0 (at T_{max} after n hours)
B	0.640	3.9×10^{15}	1.6×10^{-12} $n = 9 \times 10^{18}$
NAS ₆	0.490	9.7×10^{13}	9.6×10^{-11} $n = 3 \times 10^9$
LP	0.595	1.2×10^{10}	7.8×10^{-12} $n = 3 \times 10^5$
NS ₂	0.600	7.2×10^6	7.6×10^{-12} $n = 175$
S	0.690	2.0×10^6	1.0×10^{-8} $n = 65$
PS	0.575	1.8×10^6	3.0×10^{-10} $n = 50$

Analysis of transient effects

Governing equations

Here, the influence of transient effects upon the position and magnitude of the maximum nucleation rate will be discussed. For times where transient nucleation effects are not negligible, the position of maximum nucleation is shifted to higher temperatures (relative to the temperature of the steady state maximum) and the magnitude of the nucleation rate is reduced. This behaviour is analysed for particular choices of the steady state nucleation rate and the transient time behaviour.

If $I(t, T)$ denotes the time dependent nucleation rate and $I^0(T)$ the steady state nucleation rate, then

$$I = I^0(T)f(t, \tau) \tag{10}$$

where $f(t, \tau)$ is a function which describes the transient nucleation and depends upon the transient time, τ . The position of the maximum nucleation rate as a function of time can be found by taking the temperature derivative of Equation (10) and setting it to zero. One obtains

$$d \ln I^0/dT = x(d \ln f/dx)(d \ln \tau/dT) \tag{11}$$

where x is the time scaled by the transient time. For the transient time behaviour we choose

$$f(x) = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2x), \tag{12}$$

which is the expression derived by Kashchiev.⁽¹⁶⁾ If Equation (12) is employed in conjunction with the following form for the logarithm of the relaxation time,

$$\ln \tau = -2 \ln(T_m - T) + 2 + b/(T - T_0), \tag{13}$$

then the right side of Equation (11) becomes

$$x(d \ln f/dx) d \ln \tau/dT = [2/(T_m - T) - b/(T - T_0)^2]g(x) \tag{14}$$

and

$$g(x) = 2x \sum_{n=1}^{\infty} (-1)^n n^2 \exp(-n^2x)/f(x). \tag{15}$$

If the reduced temperature, T_r , is introduced and Equation (3) is used for the left side of Equation (11), then use of Equations (14) and (15) leads to

$$T_r + \frac{b}{(1 - T_{or}/T_r)^2} + \frac{16\pi\alpha^3\beta jh}{3} = g(x) \left[\frac{2T_r^2}{\Delta T_r} - \frac{b}{(1 - T_{or}/T_r)^2} \right]. \tag{16}$$

Solutions of Equation (16) for T_r for varying x (or t) give the location of the maximum nucleation temperature as a function of time. The steady state maximum nucleation temperature is obtained from the solution of Equation (16) with the right side of this equation equal to zero.

It will be of interest, also, to compare the maximum nucleation rate at some reduced time, x^* , with the

steady state maximum nucleation rate. If T_r^* is a solution of Equation (16) at x^* , then this ratio of maximum intensities is given as

$$\frac{I(T_r^*, x^*)}{I^\circ(T_{\max})} = \frac{I^\circ(T_r^*)}{I^\circ(T_{\max})} \cdot f(x^*, T_r^*). \quad (17)$$

If N° denotes the number of particles nucleated at some temperature when heated for some time period under steady state conditions then, since $N(t) = \int_0^t I(t') dt'$, it is possible to show that

$$\frac{N(x)}{N^\circ} = 1 + \frac{2}{x} \left[\sum_{n=1}^{\infty} \frac{(-1)^{n+1} \exp(-n^2 x)}{n^2} - \frac{\pi^2}{12} \right], \quad (18)$$

which is an expression for the reduction in the number of particles formed at a given temperature due to transient effects. The number density ratio, which is given by the ratio between the number formed at T_r and the steady state number formed at T_{\max} (i.e. the number density analogue of Equation (17)), is also of interest and is given by

$$\begin{aligned} \frac{N(x, T_r)}{N^\circ(T_{\max})} &= \frac{N(x, T_r)}{N^\circ(T_r)} \cdot \frac{N^\circ(T_r)}{N^\circ(T_{\max})} \\ &= \frac{I^\circ(T_r)}{I^\circ(T_{\max})} \\ &\quad \times \left[1 + \frac{2}{x} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\exp(-n^2 x)}{n^2} - \frac{\pi^2}{12} \right] \end{aligned} \quad (19)$$

Shift in maximum nucleation temperature

Now we employ Equations (13) and (16)–(19) to predict the shift in peak nucleation rate position and the reduction in the magnitude of the nucleation rate (and particles formed) due to transient nucleation effects. It is of particular interest to investigate the behaviour of several systems whose steady state maximum nucleation rates were predicted to fall below T_g in order to test the hypothesis that transient nucleation is responsible for the absence of homogeneous nucleation in such systems. Attention will therefore be focused primarily upon three of the compositions (NS₂, PS, and B) listed in Table 2; these were chosen because there is information in the literature regarding their crystal nucleation and growth behaviour.

First, however, we point out that the results shown in Table 2 were generated on the assumption that $\alpha = 1/2$ but if one chooses $\alpha = 1/3$, the predicted

Table 3. Predicted values for $\alpha = 1/3$

System	T_{\max}	$\tau(T_{\max})$ (s)
B	0.705	1.7×10^8
NAS ₆	0.600	2.6×10^8
LP	0.640	1.0×10^3
NS ₂	0.660	9.2×10^1
S	0.780	3.0×10^3
PS	0.675	5.0×10^0

values of T_{\max} occur at much higher values and consequently the transient times at the temperatures of maximum nucleation rate will be much smaller (compare Tables 2 and 3). In this section we consider the worst case ($\alpha = 1/2$) to analyse if transient effects can obstruct the detection of homogeneous nucleation.

Results

Na₂O · 2SiO₂ ($T_g = 723$ – 746 K)

Figure 4 shows the variation in the temperature of maximum nucleation rate with heat treatment time for NS₂ glass; there is a marked decrease in T_{\max} with increasingly longer times, reflecting the influence of transient nucleation in this temperature range (700–750 K).

The calculated values of τ and the ratio between the steady state nucleation rate at temperature T and the maximum rate $I^\circ(T_{\max})$ are shown in Figure 5. The transient period at T_{\max} (688 K) is very long but at 30 K above T_{\max} , it is reduced to about 1 h, while the steady state rate is lowered by only one order of magnitude. Hence, if the magnitude of $I^\circ(T_{\max})$ is large enough, homogeneous nucleation might be measured in NS₂ if one chooses an appropriate thermal treatment, say between 710 and 730 K for a few hours.

Crystal nucleation in a NS₂ glass (with 0.3 mol% Sb₂O₃) was sought, exhaustively, by Hishinuma⁽²⁰⁾ at 700 K for 220 h, at 770 K for 250 h, and at 820 K for

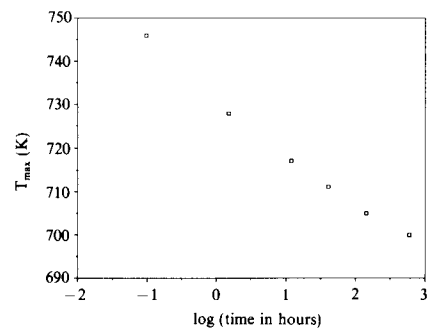


Figure 4. Temperature of maximum nucleation rate as a function of heat treatment time for NS₂ glass

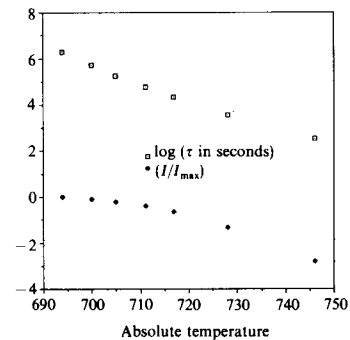


Figure 5. Calculated values of transient times and the ratio of the steady state nucleation rate at temperature, T , to the maximum rate, $I^\circ(T_{\max})$, for NS₂

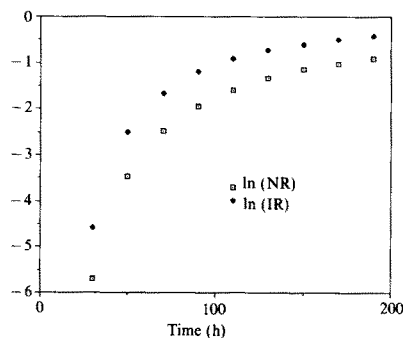


Figure 6. Ratio of predicted nucleation rate to its maximum value at 700 K for NS_2 . Similar ratio for number of crystals formed in time

140 h. For both one step and two step heat treatments crystal growth rates would have been sufficiently large to reveal any internal crystals if they existed but only surface crystallisation was observed. At 700 K, the predicted nucleation rate would approach its steady state value after about 100–200 h, even for the worst possible condition ($\alpha = 1/2$), as is shown by Figure 6, and thus homogeneous nucleation should have been detectable by Hishinuma's experiments. At the other two temperatures explored, 770 and 820 K, the transient times are much shorter, but so are the steady state nucleation rates, rendering internal nucleation unobservable.

$PbO \cdot SiO_2$ ($T_g = 674\text{--}695$ K)

Similar calculations were carried out for PS glasses, again for $\alpha = 1/2$, and Figure 7 shows the transient times and the ratio between the steady state nucleation rate at temperature T and its maximum value at T_{max} ; in this case the transient times at T_{max} (597 K) are very long. If one chooses a higher temperature, say 650 K, where τ would be greatly reduced, the steady state nucleation rates would be too much decreased, as is shown by Figure 7. At 612 K, for instance, a heat

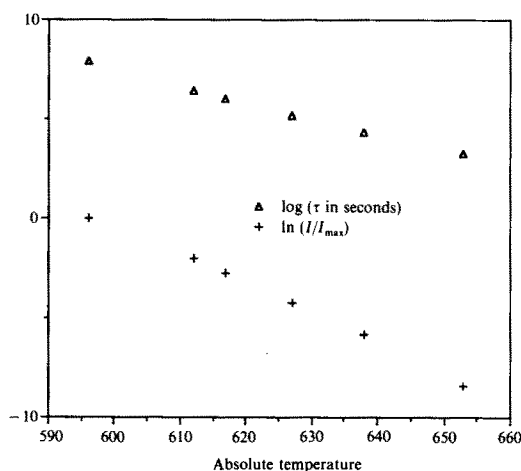


Figure 7. Calculated values of transient times and the ratio of the steady state nucleation rate at temperature, T , to the maximum rate, $I^0(T_{max})$, for PS

treatment of approximately 2000 h would be required to bring the nucleation rates (and crystal number density) to within 2 orders of magnitude of their steady state values. However, for $\alpha = 1/3$, $T_{max} = 700$ K and the transient times would be only 5 s, as is shown by Table 3.

Hishinuma⁽²⁰⁾ subjected a $PbO \cdot SiO_2$ glass to several heat treatments—at 670 K for 140 h, from 710 to 730 K for 2200 h, at 760 K for 140 h, and also at higher temperatures (780 to 900 K)—and only surface crystallisation was observed. If $I^0(T_{max})$ had been sufficiently high, internal nucleation should have been detected by Hishinuma's experiments (for $\alpha = 1/3$); for α close to $1/2$, homogeneous nucleation would not be measurable.

B_2O_3 ($T_g = 550\text{--}564$ K)

B_2O_3 is an interesting system because it has the longest induction period among the twelve compositions studied, with a T_{max} of 510 K for $\alpha = 1/3$ and 463 K for $\alpha = 1/2$. Both temperatures are well below T_g and the induction periods are extremely long, 4.6×10^4 and 10^{12} h, respectively.

For $\alpha = 1/2$ no thermal path can be found which will lead to detectable homogeneous nucleation within a reasonable time period; for the other limiting case, $\alpha = 1/3$, heat treatments in the vicinity of 530 K for 1000 h would be required if nucleation were to be detected. To the authors' knowledge, however, no one has been able to observe crystallisation (internal or surface) in B_2O_3 glass, even when the melt or the external surface has been seeded with B_2O_3 crystals. This indicates that the crystal growth rates are much too low and thus even if internal nucleation occurred, it would not be observed since the nuclei would not grow sufficiently. This is the most difficult case to analyse since τ is very long, the growth rate is extremely small, and the nucleation rate is unknown.

Other systems

Albite (NAS_6) glass also does not crystallise, even when seeded, indicating a very low growth rate. For other glasses, such as SiO_2 and P_2O_5 , the predicted T_{max} are below T_g but the transient times are such that thermal paths can be found, so that they will show homogeneous nucleation. However, SiO_2 glass, which has been extensively studied due to its commercial importance, has only shown surface nucleation and this is also true for P_2O_5 , although this has been studied much less.

Summary

The fact that homogeneous nucleation cannot be observed in glasses may be related to one or more of the following causes: low nucleation rate, low growth rate, and long induction times. It has been shown that for many oxide glasses which do not exhibit homogeneous crystal nucleation the predicted T_{max} will occur well below T_g , leading to the reasonable deduc-

tion that long induction times are responsible for this inability to detect homogeneous nucleation. However, for at least two such systems, NS₂ and PS, it has been demonstrated that temperature regions exist where the transient times are sufficiently short and nucleation rates sufficiently large to be able to detect homogeneous nucleation in a reasonable time period. Furthermore, it has been indicated that such experiments have in fact been performed and have failed to reveal any signs of internal nucleation. Hence, for at least several of the glasses which fall into the category described above, their failure to undergo homogeneous nucleation must be attributable to their low nucleation rates. SiO₂ and P₂O₅, also, probably fall into the latter class, but systematic evidence has not been compiled for these glass systems. On the other hand, B₂O₃ and albite seem to exhibit extremely long transient times (for all temperatures where *I* is not negligible) as well as vanishingly small growth rates. Both of these features appear to be related to the extremely high viscosities of these materials in the regions of their potential crystallisation.

Acknowledgements

The authors wish to express their gratitude to the Jet Propulsion Laboratory and the Division of Micro-

gravity Science and Application of NASA and CNPq for the financial support of this work. E. D. Zanotto also acknowledges Capes/Fulbright for the support of a fellowship.

References

1. James, P. F. (1985). *J. Non-Cryst. Solids* **73**, 517.
2. Neilson, G. F. & Weinberg, M. C. (1979). *J. Non-Cryst. Solids* **34**, 137.
3. Rowlands, E. G. & James, P. F. (1979). *Physics Chem. Glasses* **20** (1), 1.
4. Weinberg, M. C. & Zanotto, E. D. (1989). *J. Non-Cryst. Solids* **108**, 99.
5. Gonzalez-Oliver, C. J. R. & James, P. F. (1980). *J. Non-Cryst. Solids* **38-39**, 699.
6. James, P. F. & Rowlands, E. G. (1979). In *Phase transformations*. Vol. 2. Institute of Metallurgists, Sec. 3, p. 27.
7. Zanotto, E. D. & James, P. F. (1985). *J. Non-Cryst. Solids* **74**, 373.
8. James, P. F. (1974). *Physics Chem. Glasses* **15** (4), 95.
9. Weinberg, M. C., Neilson, G. F. & Uhlmann, D. R. (1984). *J. Non-Cryst. Solids* **68**, 115.
10. Yinnon, H. & Uhlmann, D. R. (1981). *J. Non-Cryst. Solids* **44**, 37.
11. Zanotto, E. D. & Weinberg, M. C. (1988). *J. Non-Cryst. Solids* **105**, 53.
12. Zanotto, E. D. (1987). *J. Non-Cryst. Solids* **89**, 361.
13. Gutsow, I. (1980). *Contemp. Phys.* **21**, 121; *ibid.*, 243.
14. Kalinina, A. M., Fokin, V. F. & Filipovich, V. N. (1977). *Fizika Khim. Stekla* **2**, 122.
15. Kelton, K. F., Greer, A. L. & Thompson, C. V. (1983). *J. chem. Phys.* **79**, 6261.
16. Kashchiev, D. (1969). *Surf. Sci.* **14**, 209.
17. Volterra, V. & Cooper, A. R. (1985). *J. Non-Cryst. Solids* **74**, 85.
18. Zeldovich, J. B. (1943). *Acta Phys. Chim. USSR* **18**, 1.
19. Gonzales-Oliver, C. J. R. (1979). *Ph.D. Thesis*, University of Sheffield.
20. Hishinuma, A. (1986). *M.Sc. Dissertation*. Massachusetts Institute of Technology.