

# THE ROLE OF TRANSIENT TIMES IN HOMOGENEOUS CRYSTAL NUCLEATION

Zanotto, E. D.\*, Weinberg, M. C. and Uhlmann, D. R.  
Department of Materials Science and Engineering  
Arizona Materials Labs  
University of Arizona, Tucson, AZ, USA 85712

## ABSTRACT

Employing classical nucleation theory and published viscosity and thermodynamic data, the temperatures of maximum homogeneous crystal nucleation rate,  $T_{max}$ , are computed for twelve glass-forming systems. Two distinct classes of glasses could be identified. Type 1 glasses are characterized by low reduced glass transition temperature,  $T_{gr} = T_g/T_m$ , and  $T_{max} > T_{gr}$ . These glasses possess short transient nucleation times at  $T_{max}$ . Type 2 glasses have high  $T_{gr}$ ,  $T_{max} < T_{gr}$ , and transient times are very long at  $T_{max}$ . Type 1 glasses usually exhibit homogeneous nucleation, while type 2 do not. It is hypothesized that the latter observation is due to the long transient nucleation times at  $T_{max}$  for type 2 glasses. This hypothesis is analyzed for a prototype class 2 system, sodium disilicate glass. It is demonstrated that transient nucleation effects are not responsible for the non-observability of homogeneous nucleation in this case.

## INTRODUCTION

For a number of glass compositions, large undercoolings are possible with a tolerable amount of surface crystallization in evidence. Under these circumstances, homogeneous nucleation can be explored. A number of such experiments have been performed; and homogeneous nucleation has been detected in only a small percentage of the systems studied.

In the present work, we report a trend in the results of the last experiments. Homogeneous nucleation has been reported for compositions with relatively low reduced glass transition temperature, and whose (predicted and observed) temperature of maximum nucleation rate lies above  $T_g$ . In contrast, homogeneous nucleation has not been reported for inorganic glasses for which the (predicted) temperature of maximum homogeneous nucleation rate falls below  $T_g$ . We suggest that transient nucleation effects are responsible for the lack of observability of homogeneous nucleation in the latter compositions, and analyze this hypothesis in detail.

## LOCATION OF STEADY STATE MAXIMUM NUCLEATION RATE

The steady state nucleation rate, according to Classical Theory, may be written as  $I/I_0$ ,

$$I^0 = \frac{CT}{\eta(T)} \exp(-W^*/RT) \quad (1)$$

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

In Eq. (1), C is a constant, T is the temperature,  $\eta$  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

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

$\sigma$  denotes the liquid-crystal surface energy and  $\Delta G$  is the bulk-free energy difference between liquid and crystal.

The temperature at which the nucleation rate is maximum can be obtained by solving the equation  $dI^0/dT = 0$ . If a reduced temperature,  $T_r$ , is defined as  $T_r = T/T_m$ , where  $T_m$  is the melting temperature, and  $\beta$  is the entropy of fusion in units of R, then the temperature of maximum steady state nucleation rate may be found as the solution of Eq. (3).

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

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 Eq. (3), it has been assumed that the difference in specific heat between crystal and liquid,  $\Delta C_p$ , is constant, and  $\gamma \equiv \Delta C_p/\Delta S_m$  (where  $\Delta S_m$  is the entropy of fusion). Furthermore, it was presumed that  $\sigma$  is proportional to the enthalpy of fusion  $1/\alpha$ , 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, (with b as one of the viscosity parameter constants) and for the calculations presented herein,  $\gamma$  was chosen as zero.

Table I shows the thermodynamic and viscosity data employed in the calculations. The results are shown in Fig. 1, where the reduced maximum nucleation temperatures are plotted vs  $T_g/T_m$ . The predictions are given as lines or geometrical figures rather than points. The extension along the 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  $\alpha = 1/2$  and  $1/3$  for the Turnbull ratio.

For systems in which homogeneous nucleation has been observed, the predicted values of  $T_{max}$  typically lie at or above  $T_g$ . The circles in the figure represent the experimentally determined values of  $T_{max}/T_m$  for the three systems mentioned above. For these systems,  $T_{max} \approx T_g$ . For those systems where homogeneous nucleation has failed to be detected (e.g., PS, S, B, NAS<sub>6</sub>), the predicted values of  $T_{max}$  fall below  $T_g$ .

Table I. Thermodynamic and viscosity data for several glass-forming systems

Glass	$T_m(K)$	$\Delta H_m(J/mol)$	A	B	$T_0$	
1. $Na_2O \cdot 2CaO \cdot 3SiO_2$	NC <sub>2</sub> S <sub>3</sub>	1564	87900	-4.86	4893	547
2. $Li_2O \cdot 2SiO_2$	LS <sub>2</sub>	1307	57300	1.81	1347	595
3. $BaO \cdot 2SiO_2$	BS <sub>2</sub>	1693	37000	1.83	1702	795
4. $GeO_2$	G	1387	15100	-9.94	17962	0
				-6.80	16393	0
5. $CaO \cdot Al_2O_3 \cdot 2SiO_2$	CAS <sub>2</sub>	1826	135500	-5.85	6750	738
						(1)
6. $Na_2O \cdot 2SiO_2$	NS <sub>2</sub>	1147	35500	-0.64	2315	541
			45190			
7. $Li_2O \cdot P_2O_5$	LP	926	61700	-4.10	2000	462
8. $P_2O_5$	P	853	21760	-4.87	9071	0
			27200			
9. $PbO \cdot SiO_2$	PS	1037	34000			------(2)
			60420			
10. $SiO_2$	S	1996	15000	-13.51	37157	0
				-6.88	27115	0
11. $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	NAS <sub>6</sub>	1300	55000	-8.59	21330	0
12. $B_2O_3$	B	723	22600	-5.02	3665	333

$\log(\eta) = A + B/(T - T_0)$ , (Pa.s)

(1)  $\log(\eta) = 12 - 54200/T + 61000000/T^2$

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

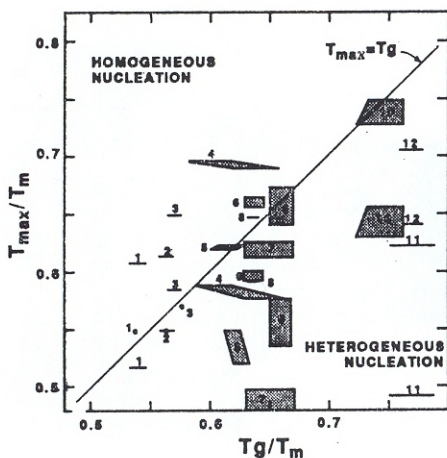


Fig. 1 Predicted reduced temperatures of maximum nucleation rates versus reduced glass transition temperature interval (lines and geometrical figures); experimental data (●).

## TRANSIENT NUCLEATION AT STEADY STATE MAXIMUM

Transient nucleation effects are a sensitive function of temperature, increasing with decreasing temperature roughly in proportion to the viscosity. Hence, for systems whose predicted maximum nucleation rates fall below  $T_g$ , one might anticipate transient nucleation effects to be important and conjecture that the non-observability of homogeneous crystal nucleation in such systems is due to the suppression of the steady state maximum nucleation rate as a result of transient effects. We illustrate this point in Table II, where the calculated  $I^0/2$  transient times at the predicted maximum nucleation rate are listed for several prototype systems. It is observed that the transient times for  $B_2O_3$  and albite ( $NS_6$ ) are particularly long. In the last column are presented the ratios of the actual (predicted) nucleation rate after heating for  $n$  hours at  $T_{max}$  to the predicted steady state rate. This ratio is quite small even after many hours of heating, and supports the hypothesis that the non-observability of homogeneous crystal nucleation in these systems is a result of transient effects. The plausibility of this argument is analyzed in more detail below.

Table II. Predicted values of  $T_{max}$ ,  $\tau$  ( $T_{max}$ ) and  $I^0/I^0_{max}$ .

SYSTEM	$T_{max}$	* $\tau$ ( $T_{max}$ ) hrs	* $I^0/I^0_{max}$ (at $T_{max}$ after $n$ hrs)
S	0.69	$5.5 \times 10^2$	$1.0 \times 10^{-8}$ ; $n = 65$
$NS_6$	0.49	$2.7 \times 10^{10}$	$9.6 \times 10^{-11}$ ; $n = 3 \times 10^9$
B	0.64	$1.0 \times 10^{12}$	$1.6 \times 10^{-12}$ ; $n = 9 \times 10^{10}$
$NS_2$	0.60	$2.0 \times 10^3$	$7.6 \times 10^{-12}$ ; $n = 175$
PS	0.60	$5.0 \times 10^2$	$2.6 \times 10^{-7}$ ; $n = 70$

\* values obtained for  $\alpha = 1/2$

## ANALYSIS OF HYPOTHESIS FOR PROTOTYPE SYSTEM

There are two factors which mitigate against the general validity of the above explanation. The  $NS_2$  composition will be chosen to illustrate these problems since experimental data are available for this material  $1/3$ . Before discussing these data, however, it is useful to consider the weakness in the above argument.

First, all the above calculations were performed for  $\alpha = 1/2$ . If one chooses  $\alpha = 1/3$ , the predicted value of  $T_{max}$  occurs at a higher value than for the choice  $\alpha = 1/2$ . Consequently, the value of the transient time at  $T_{max}$  will be much smaller. For  $NS_2$  glass,  $\tau = 92$  sec when  $\alpha = 1/3$ , compared to  $7.2 \times 10^6$  sec for  $\alpha = 1/2$ . Therefore the importance of transient time effects are critically linked to the choice of  $\alpha$ ; and if  $\alpha = 1/3$  for  $NS_2$ , transient effects will be negligible.

Consider the worst case scenario for  $NS_2$  (i.e., the longest possible transient time when  $\alpha = 1/2$ ). In this situation, the nucleation rate at  $T_{max}$  is significantly depressed for long periods of time. However, if one considers temperatures in excess of  $T_{max}$ , the transient times are much shorter, and steady state nucleation rates are reached in rather reasonable time periods. On the other hand, the magnitudes of  $I^0$  at elevated temperatures are smaller than at the maximum. This behavior is illustrated in Fig. 2. Thus, for example, at  $30^\circ C$  above  $T_{max}$  ( $T_{max} = 688K$ ), the transient time is reduced by several orders of magnitude, while the steady state rate is lowered by only one order of magnitude. Hence, homogeneous nucleation, might be measured in systems with long transient times if one chooses the appropriate thermal path. The optimal thermal path would involve heating along



the curve which describes the maximum nucleation rates at all times. This path has been calculated for NS<sub>2</sub> and for several other systems and the results are to be presented elsewhere.

Even if one does not select the optimal heating path, but chooses an isothermal path, it may be shown that transient nucleation effects would not prevent one from detecting homogeneous crystal nucleation in NS<sub>2</sub>, even if  $\alpha = 1/2$ . This may be seen from Fig. 3. Here the ratio of the nucleation rate, at  $T = 700\text{K}$ , to the steady state rate at  $T = T_{\text{max}}$  is plotted vs. time as well as the similar ratio of crystals formed in time. It may be observed that both of these ratios are in the range of  $10^{-1}$  to  $10^{-2}$  in about 100 hrs. Therefore, if the magnitude of the steady state nucleation rate at  $T_{\text{max}}$  is large enough to be observable, then homogeneous nucleation should be detectable in NS<sub>2</sub> glass via heating at  $T = 700\text{K}$  for about 100 hours.

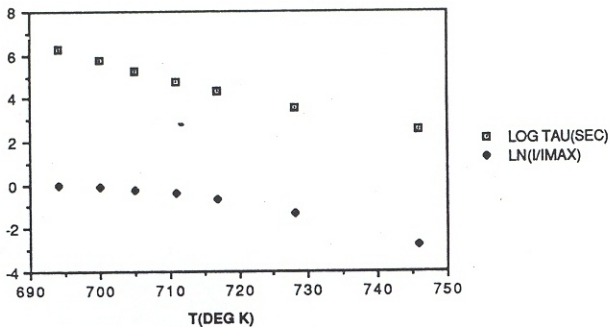


Fig. 2. Transient times and reduced steady-state nucleation rates of NS<sub>2</sub>.

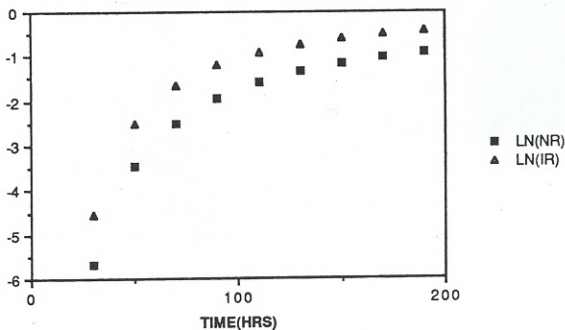


Fig. 3. Ratio of nucleation rate at 700K to  $I_{\text{max}}^0$  ( $\Delta$ )  
Similar ratio of crystals formed in time ( $\blacksquare$ ).

## EXPERIMENTAL RESULTS

As discussed above, if  $I^0$  is sufficiently high, time/temperature paths may in principle be found which lead to observable homogeneous nucleation. For  $NS_2$  glass, e.g., heat treatments at 730K for 1-2 hours should be optimum.

Crystal nucleation in a  $NS_2$  glass (with 0.3 mole %  $Sb_2O_3$ ) was exhaustively searched by Hishinuma /3/ at 700K for 2200 h, at 770K for 250h and at 820K for 140h. For both one-step and two-step heat treatments, crystal growth was enough to reveal any internal crystals if they existed. However, only surface crystallization was observed.

Since 700K is below  $T_g$ , the real transient times are expected to be 1 to 3 orders of magnitude shorter than the predicted times; and thus heat treatment for 2200 h would be enough to overcome the predicted induction period of 100h. It should also be stressed that the calculated  $\tau$  refers to the worst possible condition  $\alpha = 1/2$ . If, instead,  $\alpha = 1/3$ , the optimum temperature would be higher than 730K and the transient times much shorter. Thus homogeneous nucleation should be easily detected. Again, the experiments at 770K and 820K for long times yielded only surface crystallization.

Hence transient times alone cannot explain the lack of observable internal nucleation in  $NS_2$ ; and one must assume that the magnitude of  $I^0$  is too low.

## CONCLUSION

We have illustrated that the magnitude of the predicted transient time at the temperature of maximum nucleation is a sensitive function of the choice for  $\alpha$ . For  $\alpha = 1/2$ , transient nucleation times at  $T_{max}$  are very long for those materials characterized by  $T_g > T_{max}$ ; and this feature could prevent detection of homogeneous nucleation at  $T_{max}$ . However, at least for one such system ( $NS_2$ ), transient times decrease rapidly with increasing temperature; and homogeneous nucleation should be detectable by heating at elevated temperatures ( $T > T_{max}$ ) for reasonable times. The fact that homogeneous nucleation could not be detected by such experiments leads one to conclude that the maximum steady state homogeneous nucleation rate in  $NS_2$  is small, and that the failure to observe homogeneous nucleation in this system is not related to transient effects. Whether this is a general conclusion for this class of glasses must await further studies.

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