

## RE-EXAMINATION OF THE TEMPERATURE DEPENDENCE OF THE CLASSICAL NUCLEATION RATE: HOMOGENEOUS CRYSTAL NUCLEATION IN GLASS

Michael C. WEINBERG and Edgar D. ZANOTTO<sup>1</sup>

*Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA*

Received 14 March 1988

Revised manuscript received 29 September 1988

A comparison is made between the experimentally determined and predicted (Classical Nucleation Theory) temperature dependence of the homogeneous crystal nucleation rate in glass. Literature data for several glass-forming systems are analyzed. It is shown that the standard assumptions which are invoked to replace the free energy of activation for transport across the liquid-crystal interface,  $\Delta G_D$ , in favor of a more easily measured parameter (viscosity) are not required. It is demonstrated that  $\Delta G_D$  may be found experimentally by determining the temperature dependence of the nucleation transient time. Furthermore, it is shown that precise thermodynamic data are not necessarily required in order to make comparisons between the theoretically predicted and experimentally determined temperature variation of the nucleation rate. It is concluded that the temperature dependence of the classical homogeneous nucleation rate is still a matter of controversy.

### 1. Introduction

Crystal nucleation in glass is currently a topic of keen interest. This stems from the fact that understanding and control of the factors which affect crystallization are not only essential for many technological applications [1–3], but also are important for the synthesis of novel glasses [4,5].

During the past decade it has been recognized that the existing knowledge pertaining to crystal nucleation in glasses is quite incomplete. James [6] has recently presented an excellent review of the status of crystal nucleation in simple silicate glasses, in which the following pertinent points were made.

Nearly ten years ago Rowlands and James [7] and Neilson and Weinberg [8] compared experimental crystal nucleation data for  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  with that predicted by the Classical Nucleation Theory (CNT). Both groups concluded that there existed two discrepancies between the experimental results and CNT. First, the magnitude of the

observed nucleation rates was many orders of magnitude larger than the predicted rates. Second, although the temperature dependence of the nucleation rate could be fitted to CNT at high temperatures, at the lowest temperatures where nucleation measurements were made ( $T \leq T_g$ ) the experimental points fell below the theoretical curve.

Subsequently, crystal nucleation measurements were performed in other simple silicate glasses ( $\text{BaO} \cdot 2\text{SiO}_2$  and  $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ ) which appeared to nucleate homogeneously, and the experimental results were compared with CNT [9–11]. For the latter systems the predicted nucleation rates, once again, were found to be orders of magnitude too small, but the temperature dependences of the nucleation rates were described well by theory in all cases. These findings led Zanotto and James [12] to re-examine the temperature dependence of the nucleation rate in the  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  system. They performed careful measurements of the temperature dependence of the viscosity, and found that use of their viscosity data led to substantial improvement between experimental and CNT results for the temperature variation of the nucleation rate. Hence, it is the currently held belief that CNT provides a good

<sup>1</sup> On sabbatical leave from Universidade Federal de Sao Carlos, Brazil.

description of the temperature dependence of the homogeneous crystal nucleation rate in glasses.

The discrepancy between the experimental and theoretical values for the magnitude of the rate persists. However, James [6] has indicated that a small variation with temperature of the liquid-crystal surface tension could produce agreement between CNT and experiment for the nucleation magnitude, without destroying the accord in temperature dependence. This suggestion appears quite plausible, but to data unverified.

In the present work attention is directed upon the temperature dependence of the nucleation rate. In order to appreciate the approach taken herein, it is necessary first to review a portion of the standard arguments used to obtain the form of the CNT expression applied to crystal nucleation in glasses. The expression for the steady-state, homogeneous crystal nucleation rate,  $I^0$ , in its unmodified form, is given by [13]

$$I^0 = A(T) \exp(-[W^* + \Delta G_D]/RT), \quad (1)$$

where  $W^*$ , the thermodynamic barrier to nucleation, is equal to the free energy/mol of forming a critical nucleus,  $A(T)$  is a weakly temperature-dependent prefactor, and  $\Delta G_D$ , a kinetic barrier to nucleation, is equal to the free energy of activation/mol for atomic diffusion across the liquid-crystal interface. Unfortunately, theoretical expressions for  $\Delta G_D$  are not available. Hence, it has been common practice to introduce two separate assumptions in order to relate  $\Delta G_D$  to an easily measured experimental parameter; i.e. the viscosity. First, it is presumed that  $\Delta G_D$  can be associated with the free energy of activation for ordinary diffusion. Hence, one writes

$$D = D_0 \exp(-\Delta G_D/RT), \quad (2)$$

where  $D_0$  is constant and  $D$  is the ordinary diffusion coefficient. Next, one invokes the Stokes–Einstein equation [14], which predicts  $D \sim (kT/\eta)$  (where  $\eta$  is the shear viscosity). Via these two assumptions one obtains that the nucleation rate is inversely proportional to the viscosity.

Although there is an “intuitive feeling” that one possesses that  $I^0$  should be inversely related to  $\eta$ , neither of the latter two assumptions has ever been well justified. The Stokes–Einstein relationship is highly accurate for large particles in

liquids and has been shown to have predictive capability even for atomic motions in simple fluids, but its applicability in complex network-forming liquids has not been established. Furthermore, the identification of  $\Delta G_D$  with ordinary liquid diffusion processes is questionable. In any event, the important point that should be noted here is that these assumptions are not necessary.  $\Delta G_D$  can be experimentally determined if in addition to nucleation data, one can measure the temperature dependence of the transient nucleation time. Hence, experimental nucleation data can be compared with CNT in its “pristine” form.

Here nucleation data are analyzed using this approach. First, a description is presented discussing how  $\Delta G_D$  can be determined from the temperature dependence of the transient nucleation time. Next, the available nucleation data are analyzed. It is demonstrated that precise thermodynamic data may not be necessary in order to assess the temperature dependence of the nucleation rate. Finally, in the discussion, some of the unresolved problems are mentioned.

## 2. Theory

The classical nucleation theory for condensed systems was derived by Turnbull and Fisher in 1949 [15] and gives the steady state nucleation rate  $I^0$  as a function of the equilibrium concentration of critical nuclei  $N_c^*$  and of the rate of molecular rearrangement  $D^*$ ,

$$I^0 = Z \cdot N_c^* \cdot D^*. \quad (3)$$

In eq. (3)  $Z$  is the Zeldovich factor, given by

$$Z = \left( \frac{W^* N_a}{3\pi RT} \right)^{1/2} \cdot \frac{1}{n^*}, \quad (4)$$

where  $R$  is the gas constant,  $N_a$  is Avogadro’s number, and  $n^*$  is the number of atoms in a nucleus of critical size. The number of critical nuclei is given by a Boltzmann expression

$$N_c^* = N^0 \exp(-W^*/RT), \quad (5)$$

where  $N^0$  is the number of sites per unit volume available for homogeneous nucleation; i.e., the total number of unit cells per unit volume,  $W^*$  is the thermodynamic barrier to form a mol of criti-

cal nuclei, and  $T$  is the absolute temperature.  $D^*$  is given by

$$D^* = \frac{kT}{h} 0^* \exp\left(\frac{-\Delta G_D}{RT}\right), \quad (6)$$

where  $0^*$  is the number of atoms in the surface of a critical radius,  $k$  is Boltzmann's constant and  $h$  is Planck's constant. For isotropic, spherical nuclei

$$W^* = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta G_v)^2}, \quad (7)$$

where  $\sigma$  is the interfacial free energy and  $\Delta G_v$  the thermodynamic driving force per unit volume.

The rate of molecular rearrangement is usually assumed to be given by eq. (2), but the identification of  $\Delta G_D$  with  $\Delta G_\eta$  (the activation energy for viscous flow) and the use of the Stokes–Einstein equation have no firm theoretical sanction.

A more rigorous way to determine the kinetic barrier is by using the transient times,  $\tau$ . According to Kashchiev [16],

$$\tau = \frac{4}{\pi^3 Z^2 D^*}. \quad (8)$$

This equation has been recently tested and proved to be accurate by the independent computer simulations of Kelton et al. [17] and Volterra and Cooper [18].

Since the rates of molecular rearrangement in transient times and crystal nucleation are theoretically identical [13], the combination of equations (3,5 and 8) gives

$$I^0 = \frac{4N^0}{\pi^3 Z \tau} \exp\left(\frac{-W^*}{RT}\right). \quad (9)$$

It should be reiterated that the form of the nucleation expression given by eq. (9) does not rely upon the use of additional assumptions to eliminate  $\Delta G_D$ . The only approximation which was made was the use of eq. (8) for  $\tau$ , and as indicated above this expression for  $\tau$  appears to be nearly exact. One may take the logarithm of eq. (9) to obtain

$$\ln(I^0 \tau) = \ln\left(\frac{4N^0}{\pi^3 Z}\right) - \frac{16\pi\sigma^3}{3RT(\Delta G_v)^2}. \quad (10)$$

Since the first term on the right-hand side of eq. (10) is nearly temperature-independent, a plot of  $\ln(I^0 \cdot \tau)$  versus  $1/T \cdot (\Delta G_v)^2$  should give a

straight line \*. The intercept could then be compared to the theoretical value and the interfacial energy of the nucleus/parent phase,  $\sigma$ , could be calculated from the slope. In any case, if the predicted temperature dependence of  $I^0$ , as given by eq. (9), is correct, a straight line is obtained.

### 3. Analysis and results

Equation (10) may be rewritten in the simple form

$$\ln(I^0 \tau) = E - \frac{C}{T(\Delta G)^2}, \quad (11)$$

where  $E$  and  $C$  are positive constants. Hence, the Classical Theory predicts that  $\ln(I^0 \tau)$  should be a linear function of  $T^{-1}(\Delta G)^{-2}$ . In order to construct such plots the difference in free energy between the crystal and liquid must be known as a function of temperature. This is equivalent to requiring knowledge of  $\Delta C_p(T)$  (heating capacity per unit volume of crystal – that of liquid) since

$$\Delta G = \Delta S_m \left[ (T_m - T) - \int_T^{T_m} dT' \frac{\Delta C_p(T')}{\Delta S_m} (1 - T/T') \right]. \quad (12)$$

In eq. (12),  $T_m$  is the melting temperature and  $\Delta S_m$  is the change in entropy per unit volume upon crystallization. If one introduces the reduced temperature,  $T_r = T/T_m$ , and substitutes eq. (12) into eq. (11), then one obtains

$$\begin{aligned} \ln(I^0 \tau) = & E - C' T_r^{-1} (1 - T_r)^{-2} \\ & \times \left\{ 1 - (1 - T_r)^{-1} \right. \\ & \left. \cdot \int_{T_r}^1 (1 - T_r/T_r') \frac{\Delta C_p(T_r')}{\Delta S_m} dT_r' \right\}^{-2}, \end{aligned} \quad (13)$$

where  $C' = C T_m^{-3} \Delta S_m^{-2}$ .

\* Rigorously  $\ln(I^0 \tau \Delta G^2 / \sqrt{T})$  should be plotted to take into account the temperature term in  $Z$ . However, calculations were performed including the temperature dependence of  $Z$ , and it was found that the inclusion of this temperature dependence did not change our results on a qualitative level and, also, only had a small quantitative effect.

it is convenient to make the following definitions:

$$x \equiv T_r^{-1}(1 - T_r)^{-2}; \quad (14a)$$

$$g \equiv \left\{ 1 - (1 - T_r)^{-1} \times \int_{T_r}^1 \frac{\Delta C_p(T_r')}{\Delta S_m} (1 - T_r/T_r') dT_r' \right\}^{-2}; \quad (14b)$$

$$f = xg(x). \quad (14c)$$

Hence, a plot of  $f(x)$  vs.  $x$  may be used to generate a master curve for eq. (13). This is equivalent to a plot of  $\ln(I^0\tau)$  vs.  $x$  in the sense that the latter is shifted from and its slope at each point is a constant (negative) factor times the former. Thus, it suffices to consider the behavior of  $f(x)$ .

If  $\Delta C_p = 0$  for all undercoolings, then  $df/dx = 1$  for all  $x$ , and a plot of  $f$  vs.  $x$  will be a straight line with unit slope. If  $\Delta C_p \neq 0$ , and is a function of undercooling, then  $f(x)$  will show curvature. Thus, it appears that it is necessary to know  $f(x)$  precisely in order to test the temperature dependence of  $I^0$  as predicted by CNT. However, this is not the case. It is demonstrated in the Appendix A that for arbitrary  $f(x)$ ,  $(df/dx) \geq 1$  for all  $x$ . Thus, the absolute magnitude of the slope of a plot of  $\ln(I^0\tau)$  vs.  $x$  will always be greater than or equal to (equal to only in the limit  $T_r \rightarrow 1$ ) the slope for a similar plot in which it is assumed  $\Delta C_p = 0$ . Why is this result useful? If precise heat capacity data are not available for a given system where homogeneous nucleation measurements have been made, then one can plot  $\ln(I^0\tau)$  vs.  $x$ . If a straight line results with slope =  $-c'$ , then  $\Delta C_p = 0$  is a good approximation and the temperature dependence as given by CNT is vindicated. If for some values of  $x$  the magnitude of the slope is less than  $c'$ , then this *cannot* be attributed to an incorrect heat capacity (from the above). If the slope exceeds  $c'$ , then no conclusions can be drawn and precise  $\Delta C_p$  information is required to test the theory. Fortunately, as will be demonstrated, the observed slopes fall into these categories where judgments can be made. All that is required to perform the present analysis is  $I^0(T)$  and  $\tau(T)$  data.

Experimental data for both  $I^0$  and  $\tau$  are available for only a few glass-forming systems. This is due to the difficulty in performing nucleation measurements and transient time determinations, since a laborious and time-consuming micrographic statistical analysis usually is employed. Further complications arise due to the use of a standard double-stage heat treatment before the crystal nuclei can be optically detected, and this leads to modifications in the distribution of embryos and  $\tau$ .

In this case it should be realized that the experimental,  $\tau_{ex}$ , has two components, the real induction period  $\tau$ , plus the time  $\tau_d$  necessary to grow nuclei from the nucleation temperature,  $T_n$ , to the development temperature,  $T_d$ . Therefore,

$$\tau_{ex} = \tau + \tau_d. \quad (15)$$

It should be noted that  $\tau$  is usually obtained via the determination of  $\theta$ , the latter being the intercept of the plot of steady-state number density with the time axis. Since  $\theta$  and  $\tau$  are related by a constant multiplicative factor [17], the notation  $\tau$  will be employed. It can be easily demonstrated that  $\tau_d$  is given as

$$\tau_d = \frac{r^*(T_d) - r^*(T_n)}{g(T_n)}. \quad (16)$$

In eq. (16)  $r^*(T_n)$  is the critical radius at the nucleation temperature,  $r^*(T_d)$  is the critical radius at the development (growth) temperature, and  $g(T_n)$  is the crystal growth rate at the nucleation temperature.

In the present work  $\tau_{ex}$  values were employed since crystal growth data at  $T_n$  were unavailable for the systems considered. Hence, one must consider the possible errors introduced by this procedure, especially since Kalinina has shown that  $\tau_d$  can be non-negligible [19]. It is shown in Appendix B that the use of  $\tau_{ex}$  rather than  $\tau$  will tend to *minimize* the discrepancies found between theory and experiment in all cases.

In the present paper only those systems where both steady-state nucleation rates and transient times have been measured in the same glass will be utilized. The analysis will be divided into two categories: (1) single-component systems, where the mother (glassy) phase has the same composi-

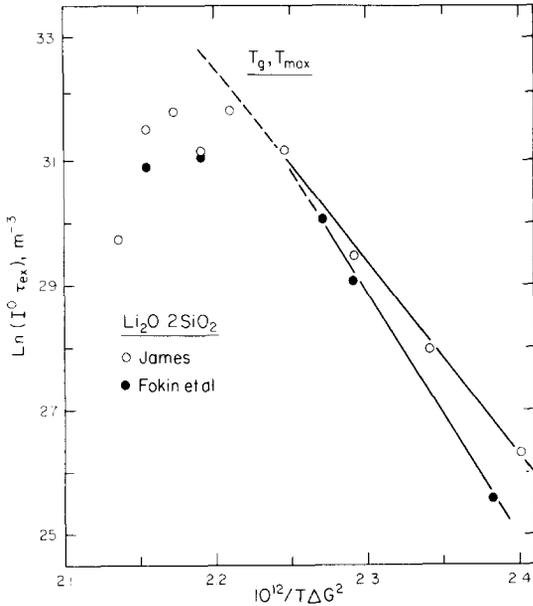


Fig. 1. Nucleation plots for  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  using the experimental data of James [20] and Fokin et al. [21]. The thermodynamic data are from ref. [23].  $\tau_{\text{ex}} = 6\theta/\pi^2$  where  $\theta$  is the intercept on the  $N_v$  versus time plots.

tion as the nucleating crystals (apart from small deviations from stoichiometry and impurities), and (2) non-stoichiometric glasses where the composition of the nucleating crystals is different from that of the parent phase.

### 3.1. Single-component systems

$\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  ( $\text{LS}_2$ ). The  $\text{LS}_2$  glass has been studied by several authors and detailed nucleation rates and induction periods are reported by James [20] and Fokin et al. [21]. For this system the thermodynamic driving force  $\Delta G$  has been determined experimentally [22,23] and therefore a complete test of theory can be made through a  $\ln(I^0 \cdot \tau_{\text{ex}})$  vs.  $1/T(\Delta G)^2$  plot, hereafter named nucleation plot.

Figure 1 shows such a plot using the experimental data of James [20] and Fokin et al. [21] for  $I^0$  and  $\tau_{\text{ex}}$  below and above the glass transition region,  $T_g$ , and the thermodynamical data given in ref. [23]. There is good agreement between the two data sets and it is clearly seen that a pronounced curvature occurs at  $T_{\text{max}}$ , the temperature of maxi-

mum nucleation rate, which nearly coincides with  $T_g$  for  $\text{LS}_2$ . Somewhat below  $T_{\text{max}}$  the slope changes sign.

$\text{NC}_2\text{S}_3$ . Nucleation rates and transient times above  $T_g$  in a  $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$  glass have been measured by Gonzalez-Oliver [24]. In this case  $T_{\text{max}}$  is  $\approx 40^\circ\text{C}$  above  $T_g$  and, again, a pronounced curvature is observed at  $T_{\text{max}}$ , as shown in fig. 2. For this glass no experimental values of the thermodynamic driving force are reported and  $\Delta G$  was approximated by the well-known expression  $\Delta H_m \cdot \Delta T/T_m$ . This implies that  $\Delta C_p = 0$ , and the use of this approximation is discussed in Appendix A.

$\text{N}_2\text{CS}_3$ . Data for a  $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$  glass have been presented by Kalinina et al. [25] and the corresponding nucleation plot is shown in fig. 3. In this case induction periods were measured from  $T_g$  ( $470^\circ\text{C}$ ) to  $T_{\text{max}}$  ( $505^\circ\text{C}$ ) and nucleation rates from  $440$  to  $550^\circ\text{C}$ . If the extrapolated data for  $\tau_{\text{ex}}$ , from a linear  $\ln \tau_{\text{ex}}$  vs.  $1/T$  plot, are used in conjunction with the measured values of  $I^0$ , in the temperature region above  $T_{\text{max}}$ , once more a change in slope is observed at  $T_{\text{max}}$ . It is easy to see that if  $\tau_{\text{ex}}$  exhibited non-exponential behavior it would be more readily observable at lower temperatures, and hence the extrapolation may be safely performed.

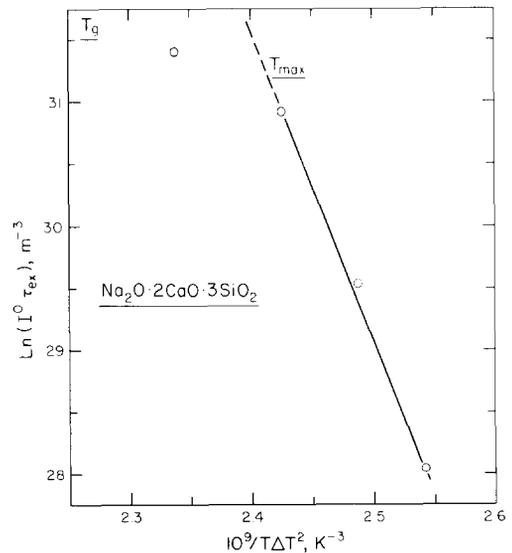


Fig. 2. Nucleation plot for  $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$  using the experimental data of Gonzalez-Oliver for glass G16 [24].

### 3.2. Non-stoichiometric systems – Approximate analysis

Glasses which crystallize with considerable changes in composition will also be considered. The analysis of nucleation plots is more complex since the thermodynamic driving force cannot be simply calculated, and thus the use of  $\Delta G \propto \Delta T$  should be used with caution. On the other hand, even in this case, the diffusional processes involved in nucleation should in principle be identical to those for transient times, and use of  $\tau$  should be preferable to viscosity in the calculation of the kinetic barrier.

$\text{Na}_2\text{O} \cdot \text{BaO} \cdot 4\text{SiO}_2$ . Burnett and Douglas [26] determined both nucleation rates and induction periods for the  $\text{BaO} \cdot 2\text{SiO}_2$  crystal phase in a  $\text{Na}_2\text{O} \cdot \text{BaO} \cdot 4\text{SiO}_2$  glass. The measurements were above  $T_g$  and included data below and above  $T_{\max}$ . Figure 4 shows a sharp break in the slope at  $T_{\max}$  and a change in sign is observed.

$36\text{Li}_2\text{O} \cdot 64\text{SiO}_2$ . The nucleation rates and induction periods of  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  ( $33.3 \text{Li}_2\text{O}$ ) crystals in a  $36\text{Li}_2\text{O} \cdot 64\text{SiO}_2$  glass have been measured by James [20]. Once more curvature is observed at  $T_{\max}$ .

Other non-stoichiometric (metallic and oxide) glasses exist where both  $I^0$  and  $\tau_{\text{ex}}$  have been measured, but only a limited range of tempera-

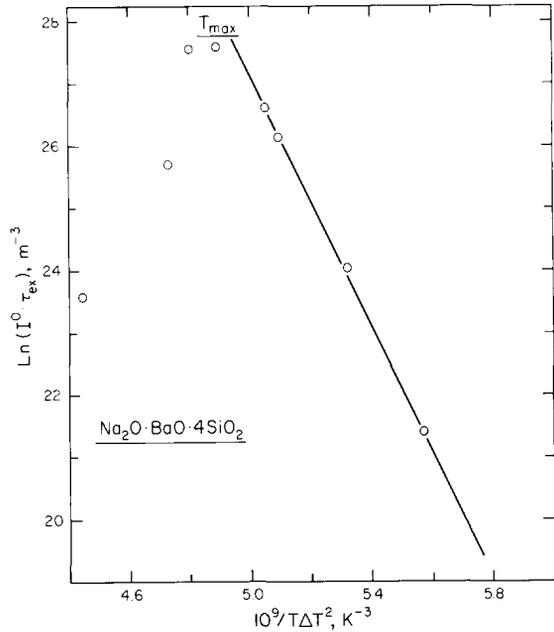


Fig. 4. Nucleation plot for  $\text{BaO} \cdot 2\text{SiO}_2$  crystals in a  $\text{Na}_2\text{O} \cdot \text{BaO} \cdot 4\text{SiO}_2$  glass. The experimental data are from Burnett and Douglas [26].  $T_g$  occurs at  $10^9/T \cdot (\Delta T)^2 = 4 \text{ K}^{-3}$ .

tures were covered which did not include data above and below  $T_{\max}$  and will not be used here.

## 4. Discussion

The most striking feature common to all stoichiometric and non-stoichiometric glasses studied is the non-linearity of the nucleation plots and the marked curvature at  $T_{\max}$ , which is considerably above  $T_g$  (with the exception of  $\text{LS}_2$ ). Therefore, complicating factors, such as abrupt changes in  $\Delta C_p$  (and consequently in  $\Delta G$ ) or in diffusion coefficients, as reviewed by Bottinga [27], which could otherwise be associated with the glass transition, are absent. Even for the  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass, where  $T_{\max} \approx T_g$  and the above-described changes are expected, the demonstration of Appendix A shows that the curvature would not be explained by changes in  $\Delta C_p$ . The most important point, however, is that for all other glasses  $T_{\max} > T_g$ .

A number of potential explanations may be offered for the discrepancies between CNT and

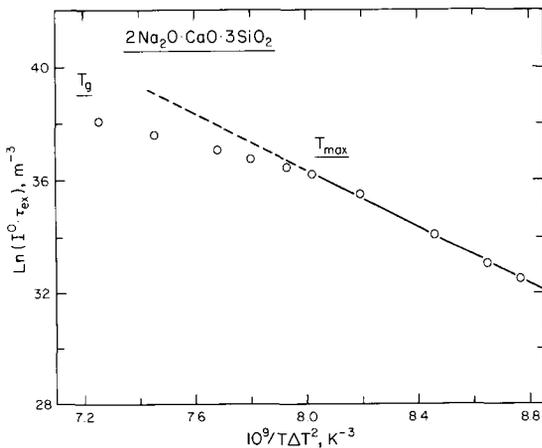


Fig. 3. Nucleation plot for  $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$  using the experimental data of Kalinina et al. [25].

homogeneous crystal nucleation data in glasses. For example, Hishinuma and Uhlmann [28] have suggested that metastable phases nucleate in anorthite, lithium disilicate, and probably in most other glasses. If this is the case, then the use of equilibrium crystal thermodynamic data would be inappropriate and could lead to errors. However, it is extremely unlikely that this suggestion could account for the divergence between theory and experiment discussed in this present work for the following reason. One could consider the nucleation of the metastable species in terms of the nucleation of some “different equilibrium state” with its own set of thermodynamic data. As discussed herein one would still expect that a plot of  $\ln(I^0\tau_{\text{ex}})$  vs.  $1/T(\Delta T)^2$  to be linear or show positive curvature.

One might believe that these results are due to errors in the measurements. However, experimental errors of  $\pm 10\text{--}15\%$  in nucleation rate determinations are mainly due to the limited statistical analysis of the micrographs, *and* due to the limited resolution of the optical microscopes, usually employed, which lead to *underestimates* of approximately  $10\text{--}15\%$ . Both kinds of errors do not depend on the nucleation temperatures and thus the variation of  $\ln I^0$  with temperature (the slope) will be susceptible to a (more or less) constant error for a given set of experimental conditions. The measurement of induction periods is subject to a more important source of error since the experimental introduction periods,  $\tau_{\text{ex}}$ , can be significantly longer than the real  $\tau$  and, in principle, the difference  $\tau_{\text{ex}} - \tau$  will depend on the nucleation temperature as shown by eq. (16). However, it is demonstrated in Appendix B that the use of  $\tau_{\text{ex}}$  rather than  $\tau$  will tend to minimize the discrepancy (non-linearity on the nucleation plots).

At low temperatures relaxation times become increasingly large and one might anticipate that non-equilibrium effects are dominant. One may crudely assess the importance of such effects by using the structural relaxation time,  $\tau_s$ , as a guide to the timescale for the structure to come to equilibrium [29]. Rekhson [30] has found that  $\tau_s$  and  $\eta$  are related by

$$\tau_s = \eta/K_p, \quad (17)$$

with  $K_p = 2.5 \times 10^{10}$  dynes/cm<sup>2</sup>. Mazurin [31] has shown that  $K_p$  varies from  $10^{10}$  to  $10^{11}$  dyn/cm<sup>2</sup> and is approximately temperature-independent. Hence, if  $K_p \approx 5 \times 10^{10}$  dyn/cm<sup>2</sup>, then  $\tau_s \approx 200$  s at  $\eta = 10^{13}$  p ( $T_g$ ). Thus, at all temperatures where nucleation measurements are made, structural relaxation times are quite short compared to transient nucleation times (many minutes) and experimental steady-state nucleation times (h). Hence, non-equilibrium effects due to relaxation phenomena are an unlikely cause for the observed disparities.

James [6] has advanced the interesting observation that allowing for a small variation of the surface tension with temperature, one can reconcile the differences between the observed and theoretically predicted magnitudes in the nucleation rates without altering the temperature dependences. Hence, one may conjecture whether a somewhat different scale to the temperature dependence of  $\sigma_{s1}$  could account for the presently observed differences. James proposed that  $\sigma_{s1}$  have the following type of temperature dependence:

$$\sigma_{s1} = \sigma_0 + aT \quad (18a)$$

and

$$a > 0. \quad (18b)$$

Eqs. (18(a, b)) imply  $(d\sigma_{s1}/dT) > 0$ . This temperature dependence would produce a larger nucleation rate at lower temperatures (see eqs. (3), (5) and (7)), however, and thus would increase the discrepancy between theory and experiment. From results on metallic systems [32,33], it appears unlikely that  $a < 0$ . Also, if  $a$  were negative the discrepancy between measured and predicted magnitudes of the nucleation rate would be far larger. Hence, it is not very probable that surface tension variations are the cause of the present dilemma, although this possibility cannot be unequivocally excluded.

Although no apparent cause for the divergence between the predicted and experimental temperature dependence of  $I^0$  can be identified, the origins of these differences are in a sense clear. Use of the temperature dependence of  $\eta$  [i.e., plots of  $\log(I^0\eta)$  vs.  $1/T(\Delta T)^2$ ] in favor of  $\tau$ , generally give good agreement with experiment. However,

while  $\tau$  maintains Arrhenius temperature dependence for all  $T$ ,  $\eta(T)$  shows significant deviations from Arrhenius behavior at low temperatures for the systems of interest. Hence, one would not expect  $\log(I^0\eta)$  and  $\log(I^0\tau)$  plots to exhibit the same temperature variation at low temperature. However, as argued herein the latter term is the quantity which appears in the original form of CNT, while  $\log(I^0\eta)$  results from the use of additional assumptions. Therefore, it is concluded that the subject of the temperature dependence of homogeneous crystal nucleation in glasses is still an unresolved question.

The authors wish to express their gratitude to the Jet Propulsion Laboratory and the Division of Microgravity Science and Applications of NASA for the financial support of this work. E.D. Zanotto also acknowledges Capes/Fulbright for a fellowship. In addition, the authors are grateful to Dr. George Neilson, of the Jet Propulsion Laboratory, for his valuable comments.

## Appendix A

It is the purpose of this appendix to demonstrate that for arbitrary temperature dependence of  $\Delta C_p$ ,  $(df/dx) \geq 1$ .

Recall that

$$f = xg, \quad (\text{A1})$$

$$g = \left[ 1 - (1 - T_r)^{-1} \int_{T_r}^1 \frac{\Delta C_p(T_r')}{\Delta S_m} \times (1 - T_r/T_r') dT_r' \right]^{-2}, \quad (\text{A2})$$

$$x = T_r^{-1}(1 - T_r)^{-2}. \quad (\text{A3})$$

Differentiating eq. (A1) one obtains,

$$\frac{df}{dx} = g + x \frac{dg}{dT_r} / dx / dT_r. \quad (\text{A4})$$

It may be shown that

$$\frac{dx}{dT_r} = T_r^{-2}(1 - T_r)^{-3}(3T_r - 1) \quad (\text{A5})$$

and

$$\frac{dg}{dT_r} = -2g^{3/2}(1 - T_r)^{-2} \times \int_{T_r}^1 \left[ \frac{\Delta C_p(T_r')}{\Delta S_m} \right] \left( \frac{1 - T_r'}{T_r'} \right) dT_r'. \quad (\text{A6})$$

Hence, employing eqs. (A5) and (A6) in eq. (A4), one finds

$$\frac{df}{dx} = g \left[ 1 - \frac{2T_r(1 - T_r)^{-1}}{(3T_r - 1)} g^{1/2} \left( \frac{\gamma_2}{T_r} - \gamma_1 \right) \right], \quad (\text{A7})$$

where

$$\gamma_1 \equiv \int_{T_r}^1 \frac{\Delta C_p(T_r')}{\Delta S_m} dT_r', \quad (\text{A8})$$

$$\gamma_2 \equiv \int_{T_r}^1 \frac{\Delta C_p(T_r')}{\Delta S_m} \left( \frac{T_r}{T_r'} \right) dT_r'. \quad (\text{A9})$$

Using the definition of  $g$  (eq. (A2)), eq. (A7) may be rewritten in a more convenient form:

$$\frac{df}{dx} = g^{3/2} \left[ 1 + \frac{[3\gamma_2 - \gamma_1]}{(3T_r - 1)} \right]. \quad (\text{A10})$$

In eq. (A9) it is clear that  $T_r' \geq T_r$ . Hence,  $1 \geq (T_r/T_r') \geq T_r$ . Therefore,

$$\gamma_2 \geq T_r \int_{T_r}^1 \frac{\Delta C_p(T_r')}{\Delta S_m} dT_r' = T_r \gamma_1. \quad (\text{A11})$$

If  $3T_r - 1 > 0$ , then  $3\gamma_2 - \gamma_1 \geq 0$ . Therefore, if  $g \geq 1$ , this will be a sufficient condition to demonstrate that  $(df/dx) \geq 1$ .

It should be noted, however, that  $T_r > \frac{1}{3}$  for all nucleation temperatures in the systems which will be analyzed herein. James [6] has observed that  $T_r \approx 0.55$  at the maximum of all these simple silicate systems. Since, as will be illustrated, the crucial temperature regime occurs just at and below  $T_r = T_{\max}/T_m \equiv T_{r\max}$ ,  $T_r > \frac{1}{3}$  is a justified condition. Furthermore, it has been shown quite generally that  $T_{r\max} > \frac{1}{3}$  [34], and therefore one may conjecture that  $T_r > \frac{1}{3}$  (over the entire temperature regime where nucleation occurs) might be a good assumption for a very large class of systems.

One may examine  $g^{1/2}$ :

$$g^{1/2} = [1 - \psi]^{-1}, \quad (\text{A12})$$

$$\psi \equiv (1 - T_r)^{-1} \int_{T_r}^1 \frac{\Delta C_p(T_r')}{\Delta S_m} (1 - T_r/T_r') dT_r'. \quad (\text{A13})$$

It is clear from eq. (A13) that  $\psi \geq 0$ . Also, it is easy to show that  $1 - \psi \geq 0$ . The latter inequality may be demonstrated as follows:

$$\begin{aligned} 1 - \psi &= (1 - T_r)^{-1} \left[ 1 - T_r \right. \\ &\quad \left. - \int_{T_r}^1 \frac{\Delta C_p(T_r')}{\Delta S_m} (1 - T_r/T_r') dT_r' \right] \\ &= (1 - T_r)^{-1} [1 - T_r - \gamma_1 + \gamma_2] \\ &\geq [1 - T_r + T_r \gamma_1 - \gamma_1] \cdot [1 - T_r]^{-1} \quad (\text{A14}) \end{aligned}$$

or

$$1 - \psi \geq 1 - \gamma_1. \quad (\text{A15})$$

However, one may readily show that  $1 - \gamma_1 > 0$ , since the enthalpy change,  $\Delta H$ , is given by

$$\Delta H = T_m \Delta S_m (1 - \gamma_1). \quad (\text{A16})$$

If  $\Delta A$  is defined as  $A_{\text{crystal}} - A_{\text{liquid}}$ , then  $\Delta S_m < 0$  and  $\Delta H \leq 0$ . If  $\Delta H$  is defined in the opposite sense then  $\Delta S_m > 0$  and  $\Delta H \geq 0$ . In either event  $1 - \gamma_1 > 0$ . Therefore,  $1 - \psi \geq 0$ . However, since  $\psi > 0$ ,  $(1 - \psi)^{-1} \geq 1$  and thus  $g^{1/2} \geq 1$ . Hence,  $g \geq 1$  and from eq. (A10) it is clear that  $(df/dx) \geq 1$ . This is the desired relationship.

Also, it is easy to demonstrate that

$$\lim_{T_r \rightarrow 1} (df/dx) \rightarrow 1. \quad (\text{A17})$$

Therefore, the high temperature slope will correspond to that of  $\Delta C_p = 0$ . Any deviations from this value of the slope at lower temperatures due to the temperature dependence of  $\Delta C_p$  will cause the magnitude of the slope to increase. The only assumption made in this derivation is that  $\Delta C_p$  does not change sign for any  $T_r$ . This appears to be a generally valid assumption.

## Appendix B

Here, it is demonstrated that use of  $\tau_{\text{ex}}$  (rather than  $\tau$ ) in the evaluation of the temperature de-

pendence of  $I^0\tau$  will not influence the net result. This follows from the fact that the magnitude of the slope in a nucleation plot will be greater for  $I^0\tau_{\text{ex}}$  than for  $I^0\tau$  (shown below). It is found that the magnitudes of these slopes are much smaller at low temperatures than predicted by CNT (see figs. 1–5), the discrepancies would be even larger if the “real”  $\tau$ 's were employed.

Using eq. (15), one can write

$$\frac{d \ln \tau}{dT_r} = \frac{1}{(\tau_{\text{ex}} - \tau_d)} \left( \frac{d\tau_{\text{ex}}}{dT_r} - \frac{d\tau_d}{dT_r} \right), \quad (\text{B1})$$

and

$$\begin{aligned} \frac{d\tau_d}{dT_r} &= - \left( \frac{[r^*(T_d) - r^*(T_r)]}{g^2} \right) \left( \frac{dg}{dT_r} \right) \\ &\quad + \left( \frac{dr^*}{dT_r} \right) \frac{1}{g}. \quad (\text{B2}) \end{aligned}$$

Since  $(dr^*/dT_r) > 0$  and in the nucleation temperature region  $(dg/dT_r) > 0$ ,  $d\tau_d/dT_r < 0$ . Hence,

$$\begin{aligned} \frac{d \ln \tau}{dT_r} &= \frac{1}{[\tau_{\text{ex}} - \tau_d(T_d)]} \left( \frac{d\tau_{\text{ex}}}{dT_r} + \left| \frac{d\tau_d}{dT_r} \right| \right) \\ &> \frac{d \ln \tau_{\text{ex}}}{dT_r}. \quad (\text{B3}) \end{aligned}$$

In appendix A it was shown that  $(dx/dT_r) > 0$  (where  $x = T_r^{-1}(1 - T_r)^{-2}$ ), therefore,

$$\frac{d \ln \tau}{dx} > \frac{d \ln \tau_{\text{ex}}}{dx} \quad (\text{B4})$$

or

$$\frac{d}{dx} (\ln I^0\tau) > \frac{d \ln (I^0\tau_{\text{ex}})}{dx}. \quad (\text{B5})$$

If the slopes remain negative in the low-temperature regime, then, from eq. (B5),

$$\left| \frac{d}{dx} \ln(I^0\tau_{\text{ex}}) \right| > \left| \frac{d}{dx} \ln(I^0\tau) \right|. \quad (\text{B6})$$

In this case use of the actual  $\tau$  would produce a less negative slope and show a *greater* departure from straight line behavior than the use of  $\tau_{\text{ex}}$ . In the event that the slope becomes positive at low temperatures, then eq. (B5) demonstrates that the actual slope will be larger (more positive) than the one computed using  $\tau_{\text{ex}}$ . The important point

which is demonstrated is that the curvature in the vicinity of  $T_{\max}$  would be even greater if the actual  $\tau$  could be utilized. Hence, the use of  $\tau_{\text{cx}}$  gives a lower limit to the departure from straight line behavior.

## References

- [1] P.W. McMillan, *Glass-Ceramics*, 2nd ed. (Academic Press, London, 1978).
- [2] D. Strand, *Opt. Eng.* 20 (1981) 379.
- [3] S.R. Ovshinsky and P.H. Klose, *J. Non-Cryst. Solids* 8–10 (1972) 892.
- [4] D.R. Uhlmann, M.C. Weinberg, and G. Teowee, *J. Non-Cryst. Solids* 100 (1988) 154.
- [5] G.F. Neilson and M.C. Weinberg, in: *Advances in Ceramics*, Vol. 5, ed. B.J. Dunbar (Amer. Ceram. Soc., Columbus, Ohio, 1983) p. 110.
- [6] P.F. James, *J. Non-Cryst. Solids* 73 (1985) 517.
- [7] E.G. Rowlands and P.F. James, *Phys. Chem. Glasses* 20 (1979) 1, 9.
- [8] G.F. Neilson and M.C. Weinberg, *J. Non-Cryst. Solids* 34 (1979) 137.
- [9] C.J.R. Gonzalez-Oliver and P.F. James, *J. Non-Cryst. Solids* 38/39 (1980) 699.
- [10] P.F. James and E.G. Rowlands, in: *Phase Transformations*, Vol. 2 (Inst. Metall., Northway House, London, 1979) sec. III, p. 27.
- [11] E.D. Zanotto, PhD Thesis, University of Sheffield (1982).
- [12] E.D. Zanotto and P.F. James, *J. Non-Cryst. Solids* 74 (1985) 373.
- [13] J.W. Christian, *The Theory of Transformations in Metals and Alloys*, 2nd ed. (Pergamon, Oxford, 1981) Part I, p. 441.
- [14] J.P. Boon and S. Yip, in: *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980) p. 154.
- [15] D. Turnbull and J.C. Fisher, *J. Chem. Phys.* 17 (1949) 71.
- [16] C. Kashchiev, *Surf. Science* 14 (1969) 209.
- [17] K.F. Kelton, A.L. Greer and C.V. Thompson, *J. Chem. Phys.* 79 (1983) 6261.
- [18] V. Volterra and A.R. Cooper, *J. Non-Cryst. Solids* 74 (1985) 85.
- [19] A.M. Kalinina, V.M. Fokin and V.N. Filipovich, *Fiz. Khim. Stekla* 2 (1977) 122.
- [20] P.F. James, *Phys. Chem. Glasses* 15 (1974) 95.
- [21] V.M. Fokin, A.M. Kalinina and V.N. Filipovich, *J. Cryst. Growth* 52 (1981) 115.
- [22] JANAF Thermochemical Tables, 2nd ed. (US Dept. of Commerce, Nat. Bur. Stand., Washington, DC 1971).
- [23] K. Takahashi and T. Yoshio, *J. Ceram. Soc. Japan* 81 (1973) 524.
- [24] C.J.R. Gonzalez-Oliver, PhD Thesis, Sheffield University (1979).
- [25] A.M. Kalinina, V.N. Filipovich and V.M. Fokin, *J. Non-Cryst. Solids* 38/39 (1980) 723.
- [26] D.G. Burnett and R.W. Douglas, *Phys. Chem. Glasses* 12 (1971) 117.
- [27] P. Richet and Bottinga, *Bull. Miner.* 106 (1983) 147.
- [28] A. Hishinuma and D.R. Uhlmann, *J. Non-Cryst. Solids* 95/96 (1987) 449.
- [29] G. Scherer, in: *Relaxation in Glass and Composites* (Wiley, New York, 1985).
- [30] S. Rekhson, *Sov. J. Chem. Glasses* 1 (1975) 417.
- [31] O.V. Mazurin, *J. Non-Cryst. Solids* 25 (1977) 130.
- [32] Y. Waseda and W.A. Miller, *Trans. Jpn. Inst. Metal* 19 (1978) 546.
- [33] F. Spaepen, *Acta. Metal.* 23 (1975) 729.
- [34] M.C. Weinberg, *J. Non-Cryst. Solids* 83 (1986) 98.