

CRYSTALLIZATION OF GLASS: A TEN YEAR PERSPECTIVE  
1993 "Vittorio Gottardi Prize" Lecture

Edgar Dutra Zanotto  
DEPARTMENT OF MATERIALS ENGINEERING  
FEDERAL UNIVERSITY OF SAO CARLOS  
13565-905, São Carlos, SP- Brazil

This paper reviews four aspects of glass crystallization: i) the effects of liquid-liquid phase separation on crystal nucleation and growth; ii) the validity of the classical nucleation theory; iii) some trends observed on homogeneous and heterogeneous nucleation in oxide glasses and; iv) the state-of-art on surface crystallization kinetics.

### INTRODUCTION

First of all I should say that it is a distinct pleasure to deliver this review lecture to such knowledgeable audience, looking at the magnificent scenery of the Greek sea (it can be seen from the lecture theater!). In this occasion, I decided to review my own work, carried out jointly with several colleges and graduate students in the past ten years, because this is a unique opportunity. However, I would like to point out that most of the research described here has been inspired in the earlier work of Russian scientists (V. Fokin, A. Kalinina and V. Filipovich), the Bulgarian group (I. Gutsow and co-workers), the Sheffield group (P. James and students), the Arizona team (M. Weinberg and D. Uhlmann) and my Brazilian colleagues (A. Craievich and E. Meyer).

I dedicate this talk to these distinguished scientists. I learned much from them. Throughout the years I discovered how one can be mentally "in phase", at least in our restricted research field, just by carefully reading a few of their papers in chronological order, listening to some of their talks and occasionally talking to them. Sometimes I try to predict what these persons are thinking or which experimental or theoretical problems they are planning to attack next. Surprisingly, I succeed several times! I guess that is how science develops. I see it (science) as a long standing game, played internationally and being slowly solved, piece by piece, year after year.

In the next sessions I will show some of the pieces I have put together in the past decade, in chronological order. I will also describe a little the history and motivation behind each research topic. Thus, this review does not cover many other important developments on crystal nucleation and growth in glass. The reader is urged to refer to the above mentioned authors if he intends to be "in phase" in the field.

This paper discusses the effects of liquid-liquid phase separation on crystal nucleation, the applicability of the classical nucleation theory to glass crystallization, some remarkable trends observed on homogeneous and heterogeneous

nucleation in oxide glasses and, finally, the state-of-art on surface crystallization. It does not review the relevant theories nor the experimental procedures due to space limitations. Here instead, I present solely a minimum of relevant equations, necessary to follow the article.

## 1. THE EFFECTS OF LIQUID PHASE SEPARATION ON CRYSTAL NUCLEATION

In the seventies there was a tremendous scientific excitement and research activity on liquid-liquid phase separation (LLPS) as well as on crystal nucleation and growth (CNG) in glasses, mainly due to the potential development of glass-ceramics having unusual properties and applications. Of special interest were the possible relationships between the two phenomena. Several authors speculated that LLPS occurred before CNG and was a necessary step for the production of fine grained glass-ceramics. A strong **controversy** on how LLPS could affect CNG existed, as shown in a meeting on "The Vitreous State" held at The University of Bristol-UK [1]. Thus, some authors defended that **compositional changes** induced by liquid phase separation could affect CNG, while others believed that the **interfaces** between the glassy phases should play an important role on crystallization, by providing favorable sites for heterogeneous nucleation.

I started working on this specific subject, as a MSc student of physics, with Aldo Craievich, in Sao Carlos, Brazil, in 1977. At the same time, Peter James had a PhD student, Anthony Ramsdem, working on the same topic in Sheffield. We exchanged some information, and after finishing my MSc dissertation in 1979, I received a grant from the Brazilian government and decided to apply to the 'Glass Mecca' at the time, Sheffield University, and there I stayed for three years as a PhD candidate. I continued working on the same topic initiated in Sao Carlos, using the excellent library and glass laboratories of Sheffield, under Peter's guidance.

We did a systematic, detailed, work with  $\text{Li}_2\text{O-SiO}_2$  and  $\text{BaO-SiO}_2$  glasses, having compositions inside and outside the spinodal and binodal areas of the respective phase diagrams. We used controlled thermal treatments to induce the simultaneous development of LLPS and CNG. The kinetics of these processes could be decoupled with SAXS, TEM and optical microscopy. The experimental details are described in [2-4]. Please note that the actual problem was raised in 1970, our research work started in 1977 and the first publication with conclusive results only came out in 1983!

### 1.1 Main Results

#### 1.1.a. $\text{BaO-SiO}_2$ Glasses:

Figure 1 shows the partial phase diagram of the baria-silica system, with the miscibility gap, glass compositions and thermal treatment temperatures used (black dots). Figure 2

shows the number of crystals nucleated at 743 C (after a development treatment at  $T_d \sim 815$  C for  $\sim 20$  min), obtained by optical microscopy associated with stereological techniques, for two glass compositions inside the miscibility gap, but outside the spinodal region. The crystal nucleation rate (curve slope) of glass 27.0 (27.0 mole % BaO) **increases** up to approximately 2 hours, which is shorter than the 7 hours period required for glasses with 28.3 mole % BaO to reach steady-state at the same temperature. The steady-state nucleation rates of the two glasses are equal, spite of their different modifier content.

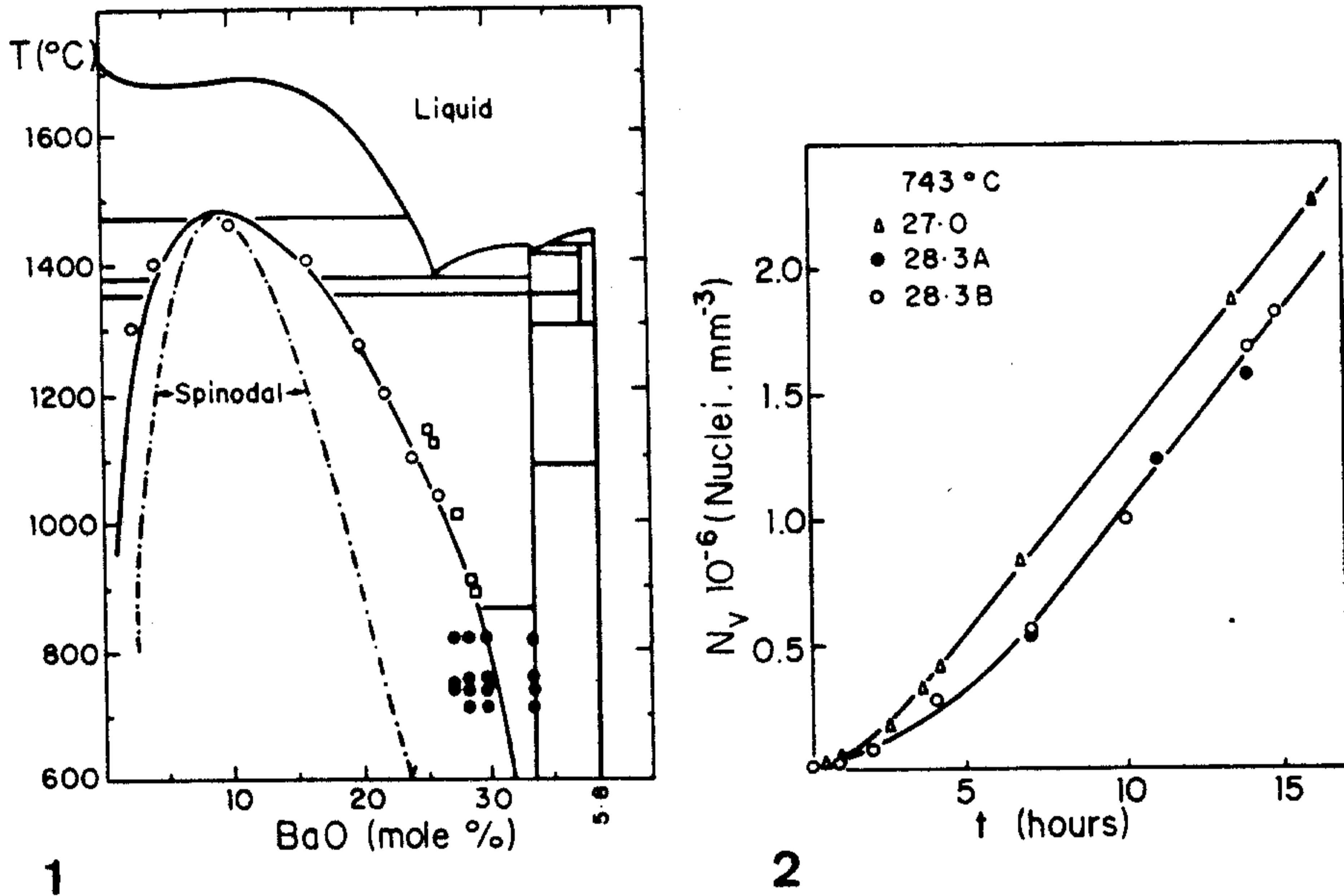


Figure 1. Partial phase diagram of the baria-silica system showing the miscibility gap (O, □) with the treatments used (●).

Figure 2. Number of crystals nucleated at 743 C in glasses with 27.0 and 28.3% BaO (A and B refer to different glasses).

The liquid-phase separation kinetics in these glasses were followed by SAXS. The scattering of X-rays was mainly due to the amorphous droplets (and not due to the crystal nuclei) because their number and electronic contrast were many orders of magnitude higher than that of the crystals. Figure 3 shows the total integrated SAXS intensity,  $Q$ , which is proportional to the electronic density contrast between the two liquid phases. Thus, when the phase separation process reaches the coarsening stage, the matrix composition reaches the equilibrium value dictated by the binodal line and  $Q$  remains invariable. The striking feature of that study is that the time required for LLPS be completed (Figure 3) coincides with

that for the establishment of steady-state crystal nucleation rates (Figure 2). Thus, the compositional effects are clear: as LLPS develops, the amorphous matrix phase gets progressively richer in Ba, and the crystal nucleation rates increase till a constant matrix composition is reached (the nucleation rate of a glass with 33.3 mole% BaO, outside the miscibility gap, is much higher). Additionally, there is no correlation between the number and surface area of the amorphous droplets and the number of crystals nucleated for all glass compositions and treatments tested. This finding eliminates the possibility that droplet interfaces play an important role on crystallization.

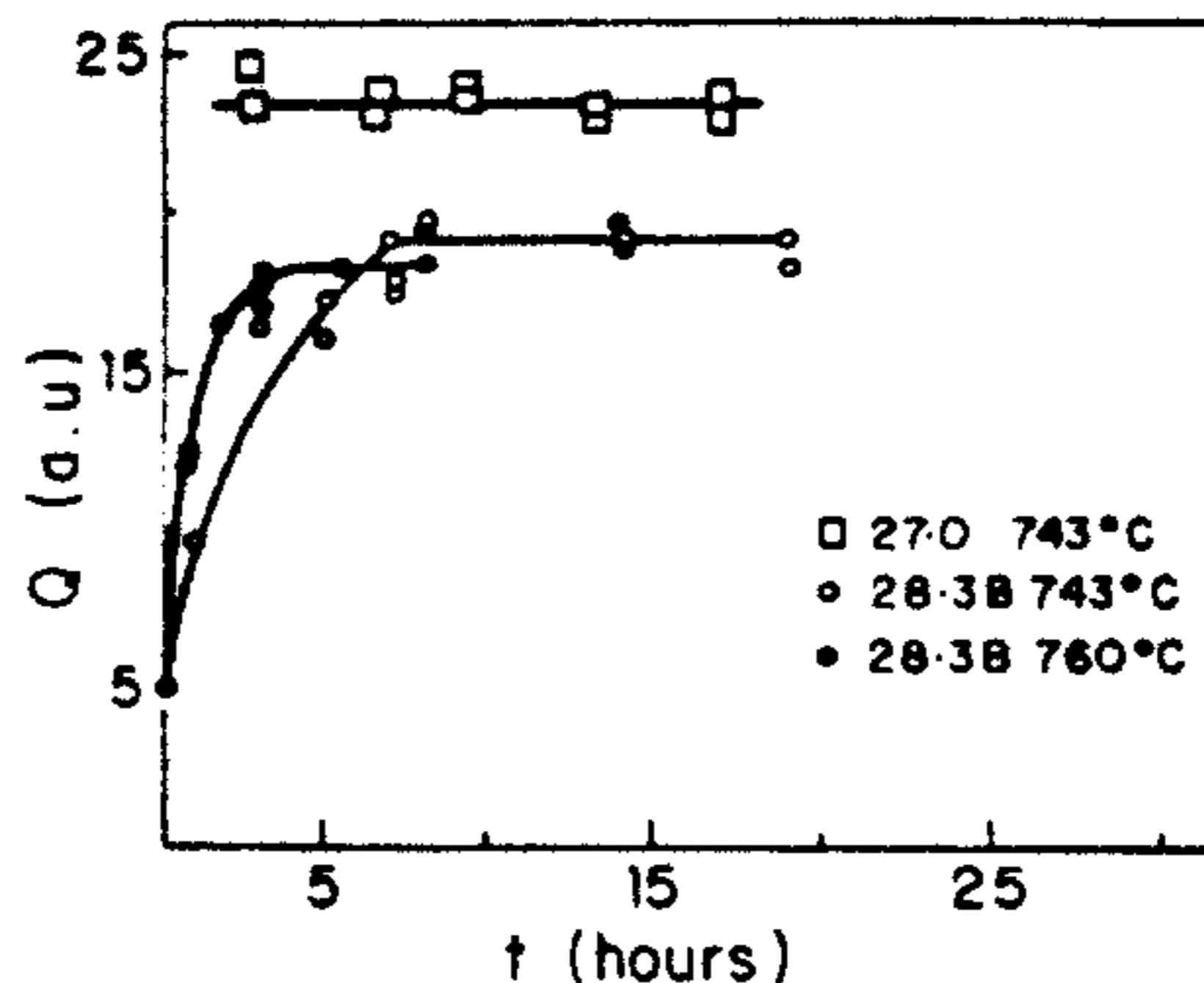


Figure 3. Total integrated SAXS intensity,  $Q$ , for the same glasses of Figure 2.

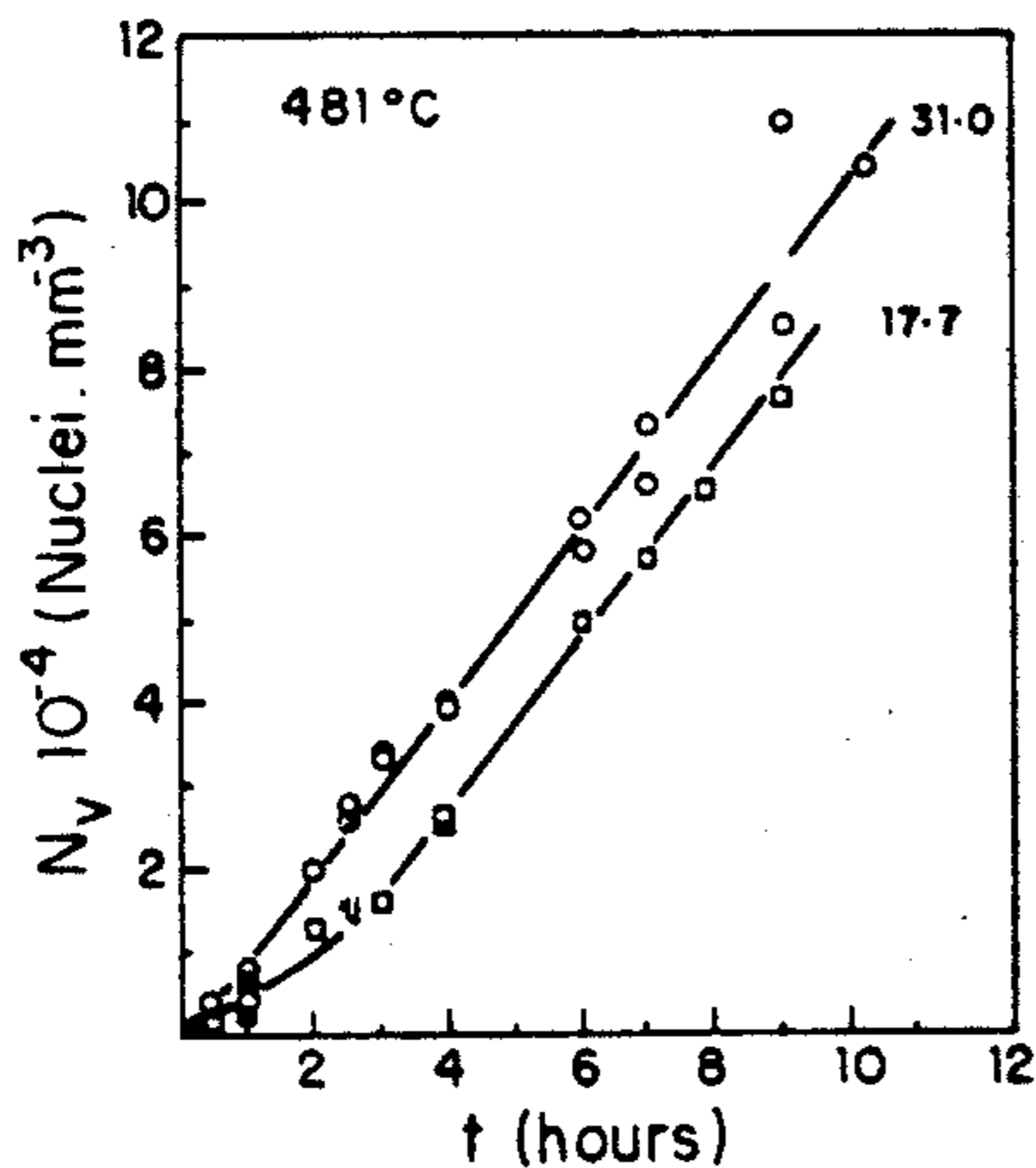
Several other experiments confirmed the overall picture shown above [4]. A limited, but conclusive, number of experiments were carried out to test the effects of LLPS on the crystal growth rates. The results were quite similar to those of the crystal nucleation experiments, being explained by the compositional effects of LLPS.

#### 1.1.b. Li<sub>2</sub>O-SiO<sub>2</sub> Glasses

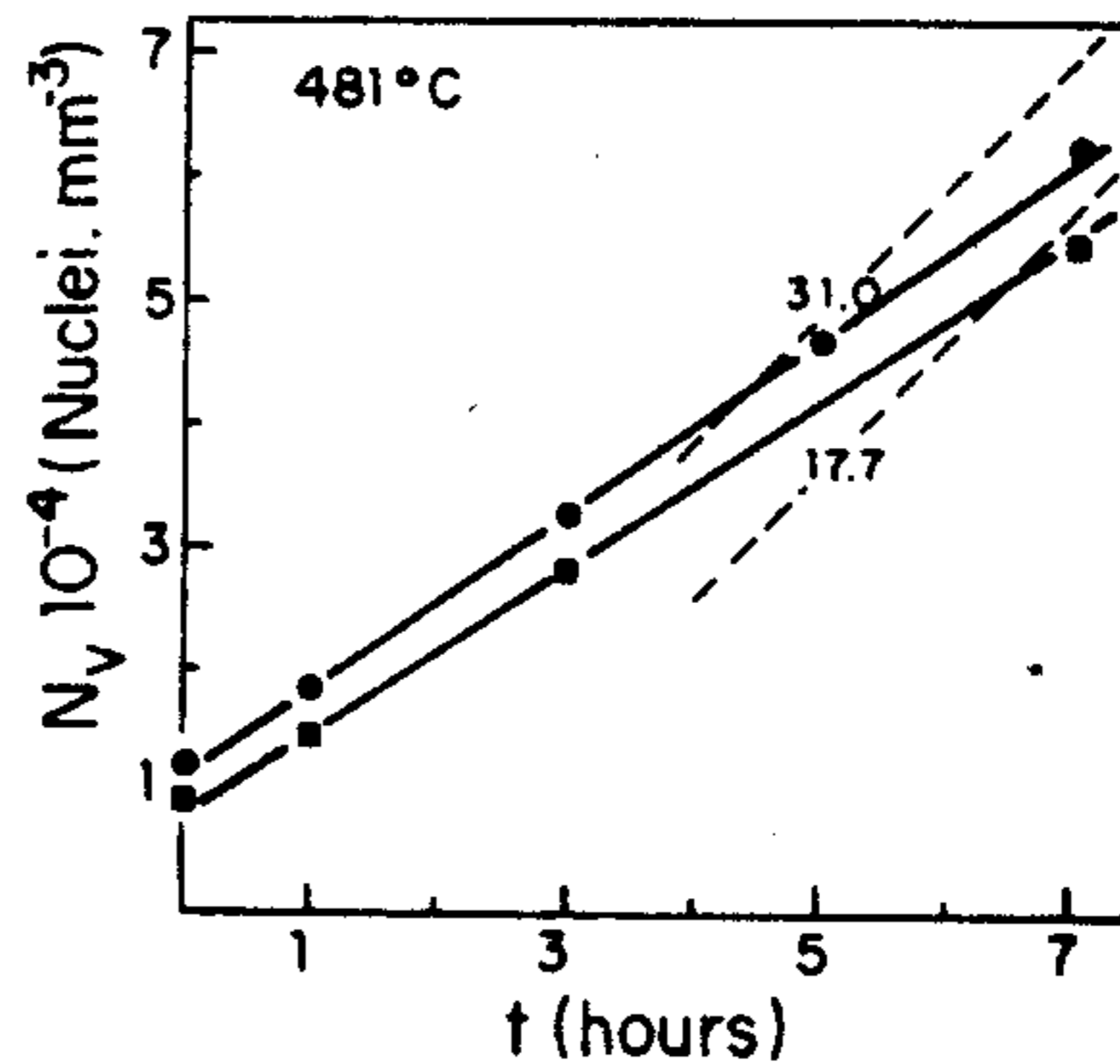
Very similar findings emerged from the study carried out with Li<sub>2</sub>O-SiO<sub>2</sub> glasses. The crystal nucleation rates for compositions having widely different modifier content, a glass with 31.0 mole% Li<sub>2</sub>O (in the nucleation and growth region of the miscibility gap) and other with 17.7 mole% Li<sub>2</sub>O (well inside the spinodal region) initially increased and then became identical when the steady-state regime was reached, after about three hours at 481 C (Figure 4). As the glass transition range is about 450 -460 C for these glasses, we concluded that the initial increase in nucleation was due to the compositional change of the amorphous matrix caused by phase separation, as in the case of Ba-glasses. When LLPS was completed, the matrix composition of the two glasses were identical (given by the binodal line) and so were the crystal nucleation rates.

A different experiment was devised to test the effects of the advanced stages of LLPS on crystal nucleation. Specimens

of the two glasses were first heated to 497 C for 5 hours to bring LLPS to the coarsening stage. After that they were nucleated at 481 C and "developed" at 570 C (the standard way to allow crystal growth to optical microscopy sizes). Figure 5 shows that the crystal nucleation rates are constant and equal from the beginning. For comparison we also plot the steady-state nucleation rates of as-quenched glasses (dashed lines). The previous treatment at 497 C eliminates the curvatures observed in the initial stages (Figure 4) and decreases the nucleation rates. The intercepts on the  $N_v$  axis are due to nucleation in the initial treatment at 497 C. The smaller nucleation rates are due to the different matrix composition of glasses which had been previously phase separated at 497 C (less  $\text{Li}_2\text{O}$ ) compared to those phase separated at 481 C. In this case, secondary phase separation has not been observed.



4



5

Figure 4. Crystal nucleation curves of glasses with 17.7 (spinodal region) and 31.0 mole %  $\text{Li}_2\text{O}$  (binodal region).

Figure 5. Crystal nucleation curves of glasses 17.7 and 31.0 previously phase-separated at 497 C for 5 h (●, ■). The dashed lines refer to the same curves shown in Figure 4.

### Conclusions

In the two glass families studied, there is a striking correlation between the time for LLPS to be completed (to reach the coarsening stage) and the establishment of steady-state crystal nucleation rates. Phase-separated glasses with widely different oxide modifier contents, but with identical glassy matrix compositions induced by phase-separation, show identical nucleation and growth rates. The number and surface area of liquid-phase droplets are many orders of magnitude higher than the numbers and surface areas of crystals for all

compositions and treatments. Therefore, the increase in crystal nucleation and growth rates are mainly due to the compositional shifts caused by LLPS. However, the observed increase in nucleation rates caused by LLPS (2-3 times) is much smaller than that due to nucleating agents (1-5 orders of magnitudes).

## 2. THE APPLICABILITY OF CLASSICAL NUCLEATION THEORY (CNT) TO GLASS CRYSTALLIZATION

Between 1971 and 1981 a series of articles were published by Kalinina & Filipovich, Matusita & Tashiro, James and co-workers and Neilson & Weinberg, on experimental tests of classical nucleation theory (CNT) using direct measurements of nucleation rates in  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  and  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{SiO}_2$  glasses; and by Uhlmann and co-workers using indirect estimates (via crystal growth rates and overall crystallization) in  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  and  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  glasses (see [5]).

Again, there was an intense dispute; a team of authors defended the validity of CNT for glass crystallization while others found enormous discrepancies between theoretical and experimental nucleation rates (from 20 to 50 orders of magnitude!). Arguments in favor and contrary included errors associated to the use of nucleation rates from one study and viscosity data from a different one (for the transport term of CNT), the possible occurrence of heterogeneous nucleation rather than homogeneous, the use of unreliable thermodynamic data or approximations for  $\Delta G$ , the initial nucleation of metastable phases, the questionable validity of the Stokes-Einstein equation for the transport term, the influence of induction periods, the possible temperature dependence of the surface energy, etc.

In 1978 James et al. [6] provided strong evidence that volume nucleation in lithia-silica glasses were predominantly **homogeneous**. In their study, glasses melted with widely different batch materials and crucibles, including platinum (a known nucleating agent for these glasses) yielded similar nucleation rates. Also, the observed maximum nucleation rates occurred at very high undercoolings,  $T_{\text{max}} / T_{\text{melt}} \sim 0.55$ , which were comparable to the maximum undercooling ever obtained for a pure element, Ga, in droplet experiments [7]. Also, reliable thermodynamic data were available for this system. Thus, Peter James and I decided to carefully remeasure both the nucleation rate curve and the viscosity of a  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass (from the same melt) having a known amount of  $\text{H}_2\text{O}$  and impurities, and retest CNT. We also performed similar experiments with a  $\text{BaO} \cdot 2\text{SiO}_2$  glass, because this composition had not been analyzed before [5].

All studies previously described assumed that the molecular rearrangements at the nuclei/matrix interfaces were controlled by viscous flow, and thus, the transport term was calculated using the Stokes-Einstein equation. Additionally, the interfacial energy  $\sigma$  was considered to be independent of nucleus size or temperature,  $\sigma = \sigma_0$ . In this case, the steady-

state homogeneous nucleation rate  $I$  is given by:

$$I = (AT / \eta) \exp( -K \sigma_0^3 / T \cdot \Delta G^2 ) \quad (1)$$

where  $A$  is a weakly temperature dependent term,  $\eta$  the viscosity,  $\Delta G$  the thermodynamic driving force and  $K$  a constant. Thus,  $\ln(I\eta/T)$  versus  $1/(T \cdot \Delta G^2)$  plots should be straight lines with  $A$  and  $\sigma_0$  given by the intercept and slope.

The results for the two glasses were very similar. The temperature dependence of the nucleation rates were well described by CNT (good straight lines), with exception of two points at the lowest temperatures, below DTA- $T_g$ , where induction times are significant and probably render underestimated values of the steady-state nucleation rates. However, the absolute values of  $I$  were about 30 orders of magnitude higher than the calculated values. Additionally, no agreement between theory and experiment could be found by varying  $\Delta G$  (even with absurd values of  $\Delta G!$ ). The only way to force agreement was by fitting a weakly temperature dependent  $\sigma$ . Therefore, our research reached similar conclusions as those of James & co-workers and Neilson & Weinberg regarding the absolute values of the nucleation rates, however, with the new viscosity and nucleation data, a better temperature dependence of  $I$  was provided by theory, even with a constant  $\sigma$

Other stoichiometric glasses (soda-lime-silica, calcium metasilicate, lithium borate, lithium metasilicate) displaying volume homogeneous nucleation, have been tested by a number of authors. The general feeling is that, in its conventional form (with a constant  $\sigma_0$ ), CNT does not predict correctly the magnitudes of crystal nucleation rates in glasses. On the other hand, the reduced surface energy or Turnbull ratio,  $\alpha$  (gram-atomic interfacial energy / molar heat of fusion) has been obtained from fitting the experimental nucleation rates of a number of glasses, and varies from 0.4 to 0.6. This range of values compares well with that of several elemental liquids, derived from maximum undercooling experiments,  $0.4 < \alpha < 0.5$  [7]. Unfortunately, however,  $\alpha$  is the unknown parameter of CNT, and has not been independently measured in glass systems so far. Therefore, one can use this range of  $\alpha$  to estimate the temperature dependence (but not the magnitude) of nucleation rates in undercooled liquids.

Thus, the most probable causes of discrepancy between theory and experiment are: i) the initial precipitation of metastable phases, a common phenomenon in glass crystallization; ii) the use of viscosity to calculate the transport term of CNT and iii) the assumption that the surface energy is that of a macroscopic crystal,  $\sigma = \sigma_0$ .

Taken into account that  $\sigma$  comes out from fitting theory and experiment, its value automatically reflects the nucleating phase stability. Additionally, the diffusion process in crystal nucleation is dictated mainly by atomic transport in the glass (matrix) phase, and thus do not depend on the nature of the nucleating phase. Hence, we discarded the

first possibility. We came to this conclusion because even using absurdly large or small values of  $\Delta G$  (possible associated with the precipitation of metastable phases) would not bring theory and experimental data into accord. Therefore, we decided to check the second possibility, by carrying out a more rigorous test of CNT, using the **induction periods** rather than **viscosity**, to account for the transport term. This eliminates the assumption that viscous flow controls the atomic transport for nucleation because, in principle, whatever diffusional mechanisms are involved in steady-state nucleation, they should be the same that control the induction times in non-steady-state nucleation. Thus, CNT reads:

$$I = (A' / \tau) \exp(-K \sigma_0^3 / T \Delta G^2) \quad (2)$$

where  $\tau$  is the temperature dependent induction period and the other parameters were defined before. Thus, one can fit the independently measured values of  $I$ ,  $\tau$  and  $\Delta G$  to Equation (2) to obtain  $A'$  and  $\sigma_0$  [8].

This type of calculation was performed for a number of glasses [8], however, the temperature dependence and magnitudes were not well described by Equation (2). The disagreement was even worse than for the previous tests, using the viscosity (Figures 6 and 7).

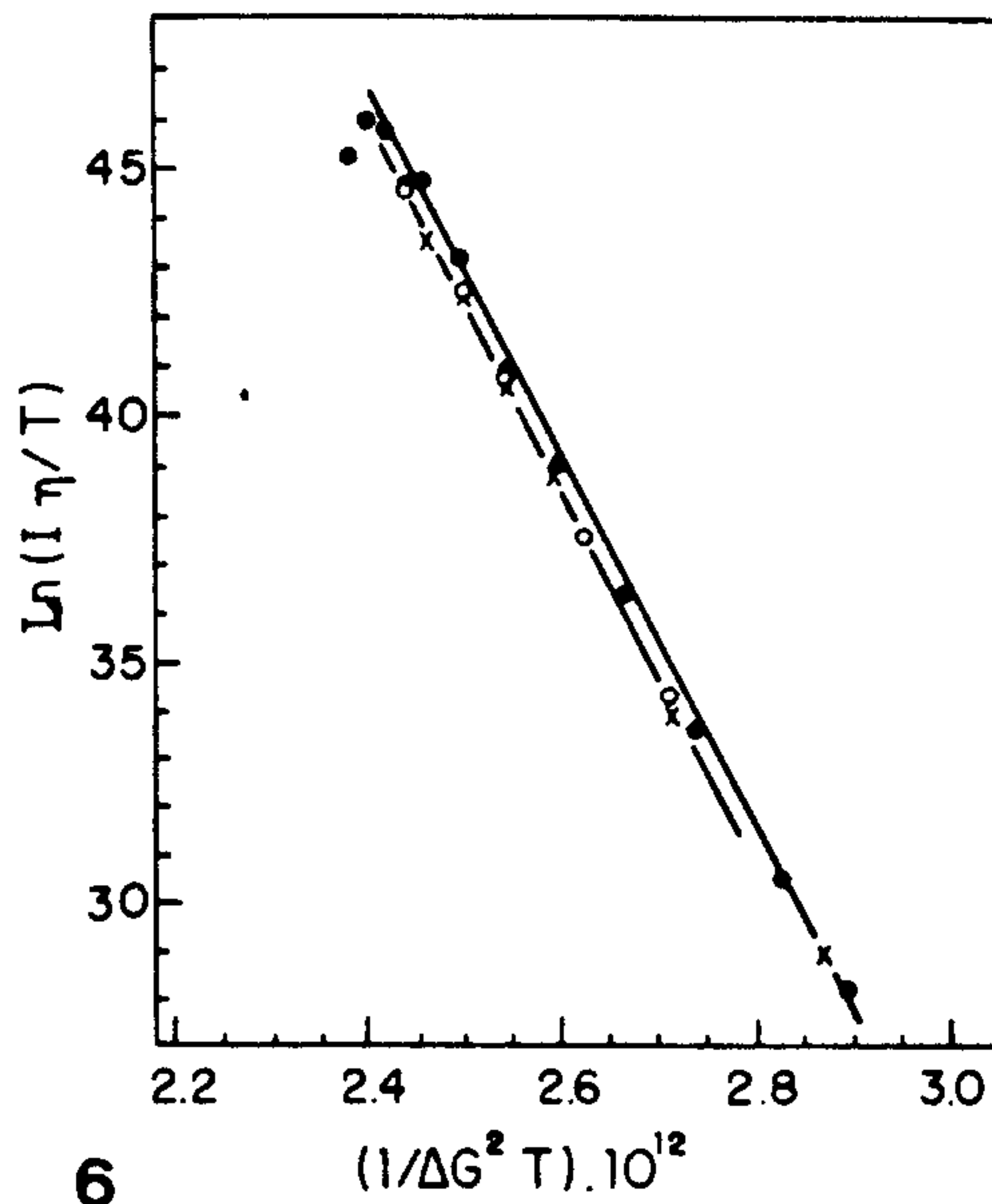
The third possibility is to assume a size or temperature dependent surface energy. In three occasions [9-11] we took Tolman's equation for  $\sigma(r)$  and rederived CNT with this different view. Tolman's equation reads:

$$\sigma(r) = \sigma_0 / (1 + \lambda/r); \quad \lambda \ll r \quad (3)$$

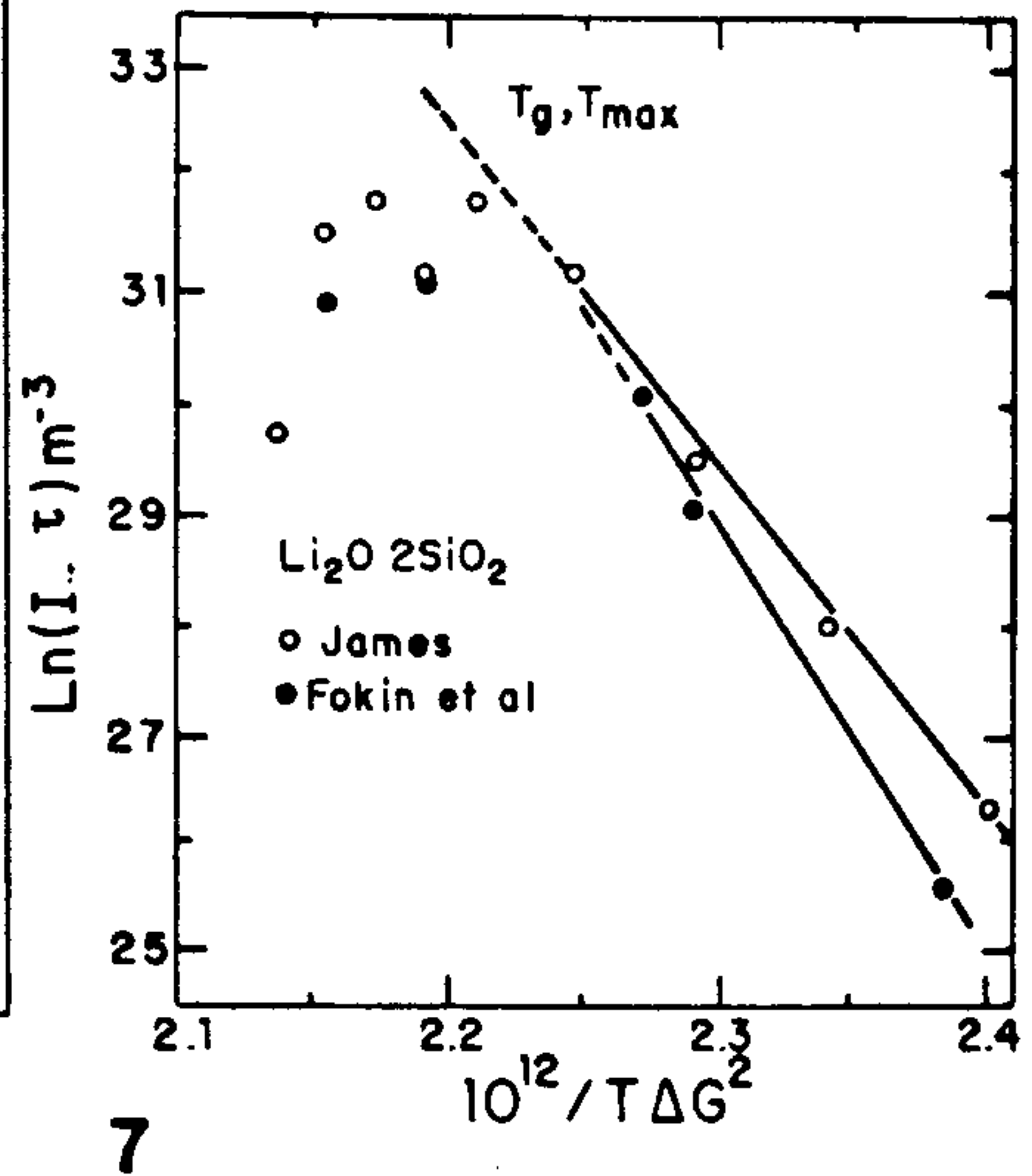
where  $\lambda$  has the order of a molecular distance. This equation overestimates the surface tension by  $\sim 7.5\%$  when  $\lambda = r$ .

The new form of CNT, denominated curvature dependent classical nucleation theory (CD-CNT), has different pre-exponential and exponential terms from those of Equations (1) and (2) and were described in [9-11]. The problem now is the additional unknown parameter,  $\lambda$ . One may reasonably assume that  $\lambda$  is equal to the lattice parameter of the nucleating crystal, and follow the same procedure used with CNT, i.e. to fit experiment to theory as to make the maximum nucleation temperatures to coincide (CD1) [9]. However, one may instead, leave  $\lambda$  to be adjusted by force fitting CD-CNT to agree with both the magnitude and temperature of maximum experimental nucleation rate (CD2) [10, 11].





6



7

Figure 6. Nucleation plots for  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glasses according to Equation (1). Nucleation data from different authors ( $\bullet$ ,  $\circ$ ,  $\times$ ) described in [5]. SI units are employed.

Figure 7. Nucleation plots for  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  according to Equation (2). Steady-state nucleation rates,  $I$ , and induction times,  $\tau$ , from James and Fokin et al., described in [8].

Figure 8 shows the experimental and theoretical nucleation rates of  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  calculated by CNT and CD-CNT in the two ways above described. The discrepancies between experiment and theory decreased considerably (from 30 om with CNT to 6 om with CD1). The calculations with CD2 cannot be compared to experiment because both the magnitude and position of the peak were used in the mathematical fitting. Even with this force fitting, the temperature dependence of  $I$  is not perfectly described.

Figure 9 shows the variation of  $\sigma$  with temperature, obtained by force fitting the standard form of CNT to experiment (a procedure first used by Turnbull). It also shows the temperature dependence of  $\sigma$  obtained by forcing both the temperature and magnitude of maximum nucleation rate given by CD-CNT to agree with experiment. The size dependence of  $\sigma$  was transformed into temperature dependence. The interesting conclusion is that both methods show a moderate increase in  $\sigma$  with temperature. The challenge now is to devise a way to **measure**  $\sigma$  at a sufficiently high  $T$ , where the critical nucleus size is large enough. One possible way, is to find a glass (or polymer) whose crystal growth mechanism is via **2-D secondary nucleation**, to determine  $\sigma$  from the fit to the growth rate curve at low undercoolings and compare that value with the extrapolated ones, obtained from nucleation experiments at much lower temperatures.

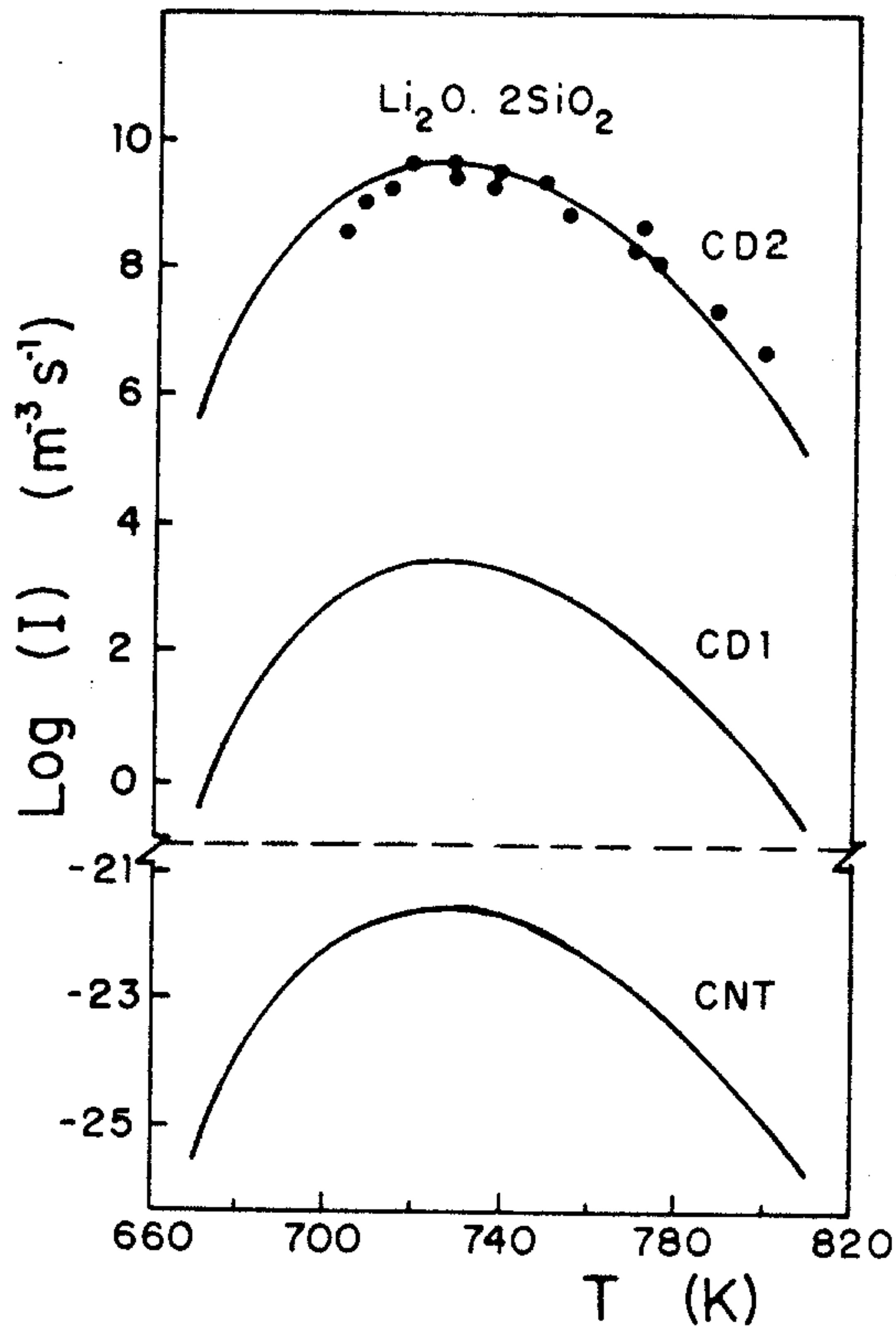


Figure 8. Crystal nucleation rate curves of  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  calculated by CNT, CD1 and CD2. Experimental data of James (●). Calculations of [10].

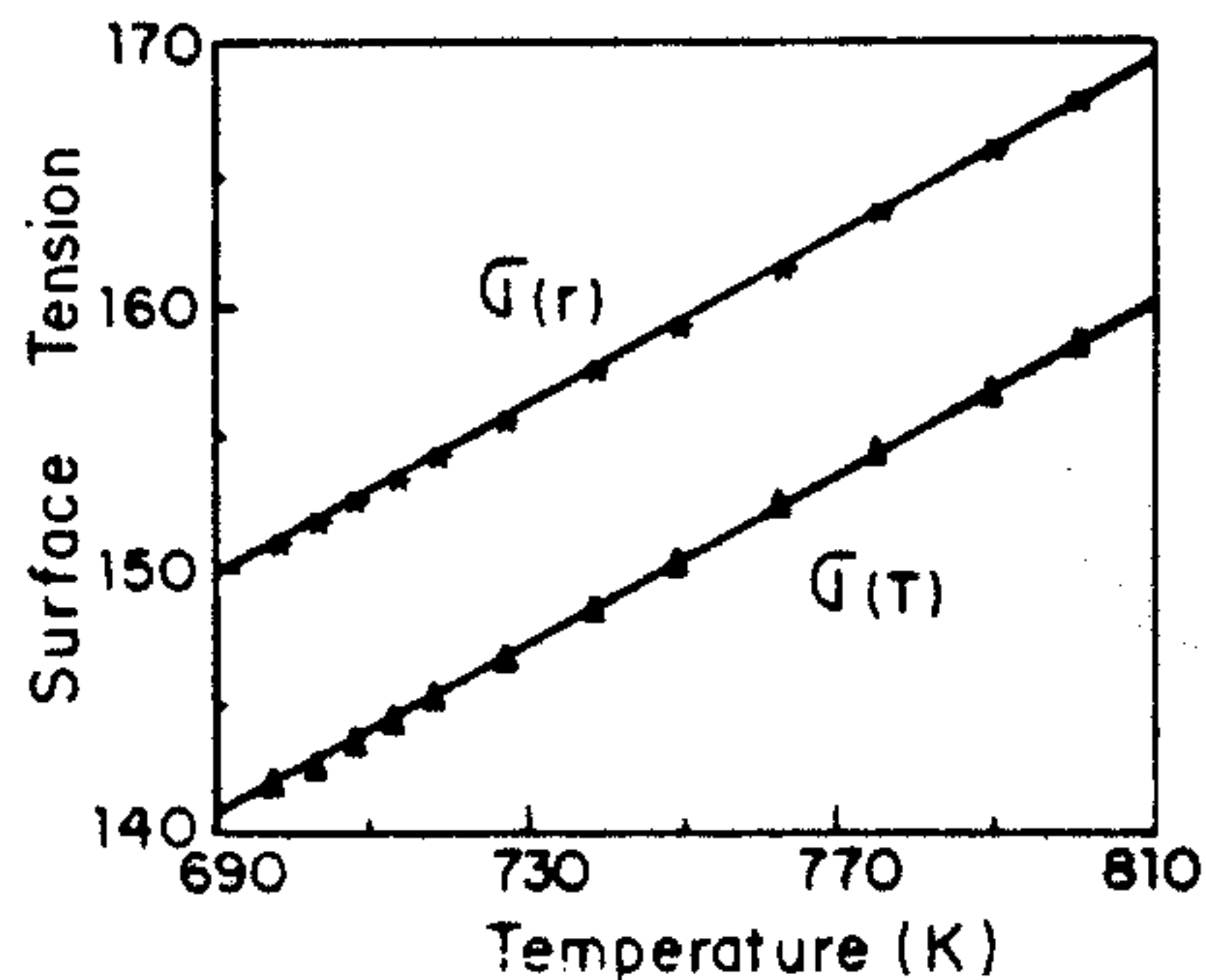


Figure 9. Temperature dependence of surface tension,  $\sigma$ , used by James to fit CNT to the nucleation data of Figure 8, and effective temperature dependence of  $\sigma$  found using a radius dependent surface tension, CD2 [11].

## Conclusion

CNT is not capable of quantitatively predicting homogeneous nucleation rates in glasses when a constant surface energy is used. It works much better when a size and/or temperature dependence of  $\sigma$  is taken into account. However, since this parameter cannot be evaluated independently, a main uncertainty still exists concerning the validity of CNT.

## 3. TRENDS IN CRYSTAL NUCLEATION IN GLASSES

Some reasonably good glass forming systems, even in the absence of nucleating agents, show a remarkable nucleation behavior, ie. volume nucleation is easily detected by optical microscopy at high undercoolings ( $T/T_m \sim 0.5-0.6$ ), and the nucleation rates are only moderately dependent on impurity level. That has been assumed to be a strong sign of homogeneous nucleation. On the other hand, the vast majority of glasses only show surface and catalyzer induced, heterogeneous nucleation. Then, intriguing questions arise: Why some glasses nucleate homogeneously? Do these glasses have any special features?

With that problem in mind, and following a hunch given by James [12], we collected literature data and reported some **trends** observed in the experimental nucleation behavior of stoichiometric oxide glasses [13, 14]. These glasses could be divided in two classes: The first family shows homo-nucleation, which has only been observed for compositions having low reduced glass transition temperatures,  $T_g/T_m < 0.6$ , and whose temperatures of maximum nucleation rates,  $T_{max}$ , lie in the vicinity of  $T_g$  (DTA  $T_g$ ). On the other hand, the second family shows only hetero-nucleation, ie. homogeneous nucleation has not been reported for compositions whose  $T_{max}$  (predicted by CNT, with reasonable values of  $\alpha$  and  $\Delta G$ ) occurs well below the glass transition range. Figure 10 exemplifies the trend, and allows one to distinguish the two families, oxide glasses displaying homo-nucleation (1.  $Na_2O.2CaO.3SiO_2$ , 2.  $Li_2O.2SiO_2$ , 3.  $BaO.2SiO_2$ ) from those showing hetero nucleation (7.  $Li_2O.P_2O_5$ , 9.  $PbO.SiO_2$ , 10.  $SiO_2$ , 11.  $Na_2O.Al_2O_3.6SiO_2$ , 12.  $B_2O_3$ ). The numbers are the same used in [14], but some data has been omitted for clarity.

Seeking some reasonable explanations for that behavior, we estimated (using the Kaschiev equation and viscosity data) that quite **long induction times** were necessary before nucleation could be detected in all cases of hetero-nucleation, ie glasses having (predicted)  $T_{max}$  well below  $T_g$ . An additional possibility is that the steady-state homogeneous nucleation rates are very low for this second family, however, this last point cannot be proved due to the insufficient predictive power of CNT.

E. D. Zanotto

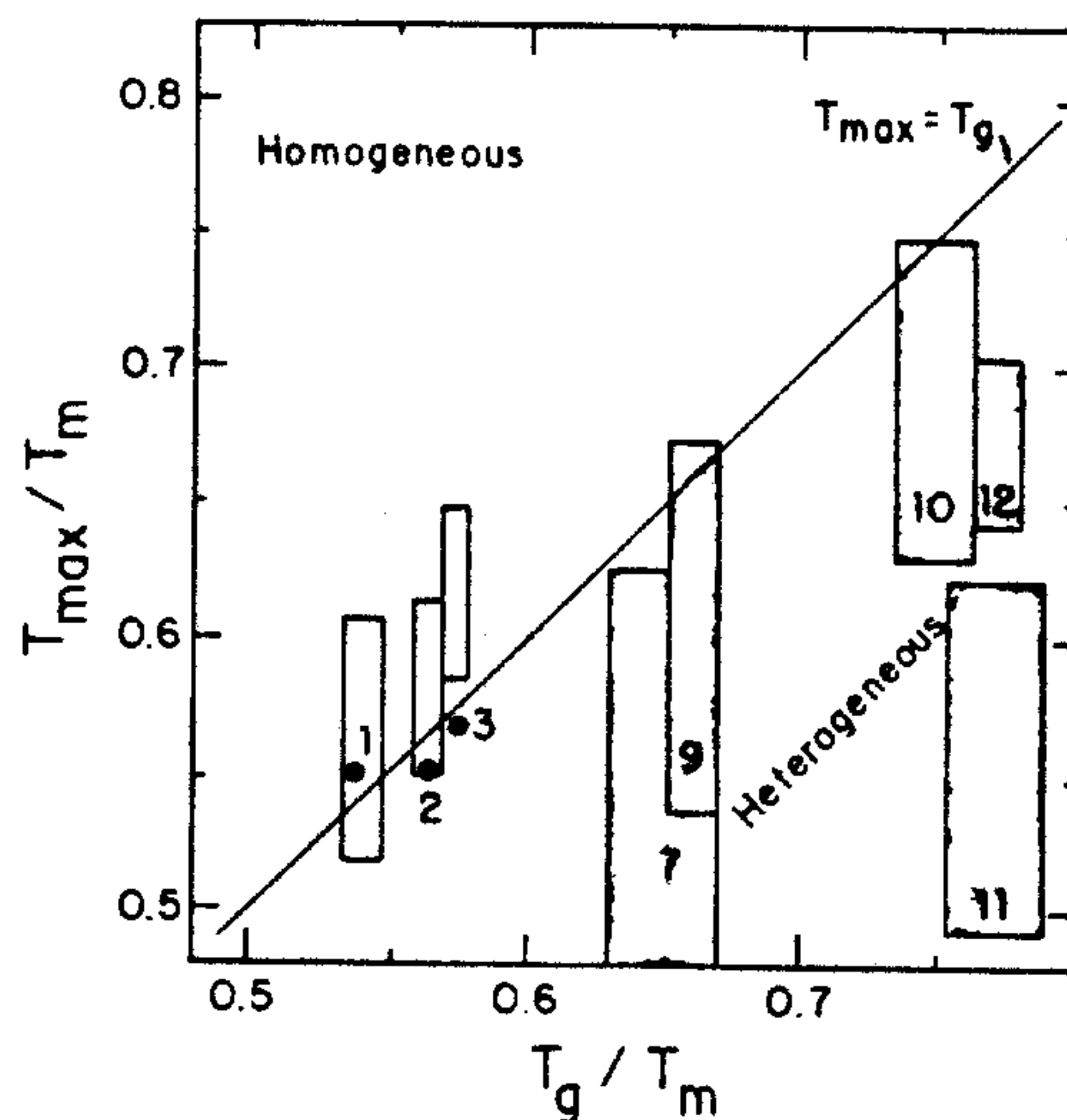


Figure 10. Calculated values of reduced temperature of maximum nucleation frequency against reduced glass transition temperature interval. (•) Experimental data.

Hence, it was clear that two classes of glasses exist. A final point regarding the trends, was provided by two studies aimed to solve the following questions: Are there any relationships between the molecular structure of supercooled liquids and their iso-chemical crystal phases? How could such relationships dictate the nucleation mechanism?

In [15] we looked at the molecular structure of glass and iso-chemical crystal phases, from both **cationic** (short range order around the alkali modifier) and **anionic** ( $\text{SiO}_4$  tetrahedra distribution in terms of single-bonded Oxygens) points of view in several stoichiometric silicate glass compositions. We demonstrated that for six glasses belonging to the first family, which nucleate homogeneously, both cationic and anionic arrangements of glass and crystal are quite similar. For five compositions belonging to the second family of glasses, the structures of glass and crystals are different and only hetero-nucleation is observed.

Additional evidence for structural similarity of glass and crystal phases in glasses of the first type was given in [16]. In that paper we demonstrate that the mass densities of glass and crystal do not differ by more than ~ 8% for those glasses, while the differences can be as high as 33% for the second family of glasses. Thus, we concluded that similar densities of glass and crystal is a necessary, but not sufficient, requirement for structural similarity and inferentially for homo-nucleation.

## Conclusion

The questions previously formulated may be answered as follows: Some glasses nucleate homogeneously in laboratory time scales because the short range cationic and anionic arrangements of their glassy and crystal phases are quite similar. Hence, the surface energy ( $\sigma$ ) is sufficiently small as to make the nucleation rates measurable at sufficiently low temperatures, but at or above  $T_g$ , where the induction periods are not longer than a few minutes. For the other glasses, even the local atomic arrangements of glass and crystal phases are distinct, which make  $\sigma$  large and move the nucleation curve to higher undercoolings, below  $T_g$ , where long induction times render the experimental detection of nucleation unfeasible.

## 5. SURFACE CRYSTALLIZATION OF GLASSES

Surface crystallization is much more frequent than volume crystallization, but much less is known about this phenomenon. Most studies carried out until 1986 were of qualitative character and only (plausible) speculations existed on the mechanisms of surface crystallization.

That year, I decided to attack this problem by giving some of my graduate students the task of measuring nucleation and growth rates at free glass surfaces. By occasion of the International Congress on Glass in Leningrad in 1989, I proposed to the Devitrification Committee of the ICG, TC 7 (now Crystallization Committee) to carry out a systematic study on this subject. The proposal was accepted and the chairman, Wolfgang Pannhorst, prepared specimens of cordierite glasses which were shipped to the committee members: myself, M. Yamane (Japan), I. Mac Donald (UK), I. Szabo (Hungary) and W. Holland and K. Heide (Germany). Wolfgang also sent specimens to Ralf Muller (Germany), who had just finished his PhD Thesis on crystallization kinetics of cordierite glasses [17]. This international group of people is still working on the subject and meet every year to discuss and exchange information. The next meeting is planned to happen in conjunction with the Otto-Schott Colloquium, in Jena (July, 1994).

To my surprise, the first data set obtained by my students in 1986, on the number density of surface crystals  $N_s$  (crystals/unit area), in mechanically polished specimens of a diopside glass, a composition which does not show volume nucleation, did not vary with time of heat treatment at 820 C ( $T_g \sim 730$  C). The scatter in  $N_s$  (50%) was much larger than that typical of volume nucleation measurements (10%). The evolution of overall surface area crystallized was quite well described by the Kolmogorov-Avrami equation, without recourse of any adjustable parameter, for the case of **instantaneous nucleation from a constant number of sites**. Hence, surface nucleation reached saturation in the early stages.

Another research was carried out with a microscope slide glass [18], and the effect of the surface condition was tested

by using three types of specimens: as-received, mechanically polished and fire-polished samples treated from 715 to 1000 C ( $T_g \sim 550$  C) for time periods of up to 30h. Figure 11 shows the dependence of the number density of devitrite crystals with time, temperature and surface condition. As for diopside, there was a large scatter in the experimental values, specially for the as-received specimens. However, for a given surface treatment these values were insensitive to variations in heat treatment! The effect of surface condition was clearly dominant. Another surprising result was that fire-polished samples did not show any crystals at 730 C up to 7.5 hours!

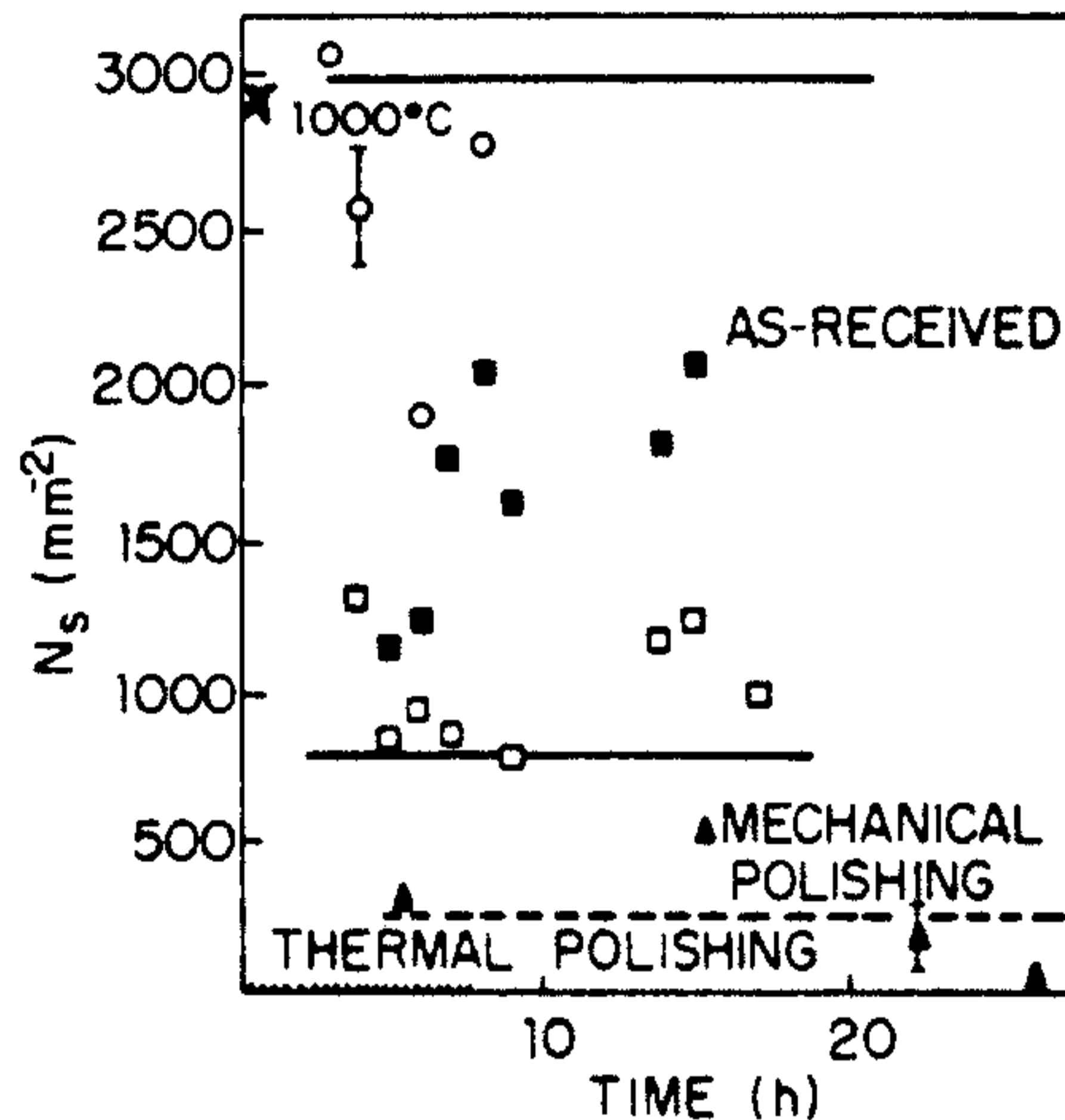


Figure 11. Crystallite density of devitrite on the surface of a microscope slide glass. As-received surfaces 715 C (o), 730 C (■), 735 C (□) and 1000 C (x) [18].

At that time, 1988, I was reluctant to publish the results presented above, mainly due to the unexpected time and temperature insensitivity of  $N_s$ . I finally decided to present them at the IV Otto-Schott Colloquium in Jena, in 1990, to a skeptical audience. However, to my surprise, in that same Colloquium, Ralph Muller had a poster showing a very similar behavior of fractured surfaces of cordierite glass. No time or temperature variation in the number of  $\mu$ -cordierite crystals was observed for a wide range of thermal treatments.

All studies of surface crystallization described so far used single-stage thermal treatments. The final shot came from Kalinina et al. [19], who used the standard double-stage treatments in a cordierite glass, from 140 to 860 C ( $T_d=933$  C for 1.5h) for periods up to 450 h! Again, the number density of  $\mu$ -cordierite crystals were time and temperature independent, confirming the other studies. However, another phase, x-phase, did show a different temperature dependence, i.e., a bell shaped curve, similar to volume nucleation curves. Thus, in at least one case (x-phase) the surface nucleation rates were sufficiently small to be measured. A summary of the most relevant studies up to 1992 is given in [20].

## Conclusions

The surface nucleation sites saturate in the early crystallization stages. Thus  $N_s$  appears to be constant. In most cases, the surface nucleation rates are too fast to be measured in wide temperature ranges, from  $T_g$  to  $T_m$ . This insensitivity to temperature is probably due to the small value of surface energy associated to heterogeneous nucleation. Hence, the Turnbull ratio,  $\alpha$ , is expected to be smaller than 0.3, because in this case, the nucleation parabola should be quite flat. No crystallization is observed on pristine, clean, surfaces or internal bubbles, as predicted by simple thermodynamic arguments. Surface nucleation is mainly due to contamination of solid particles, whose number is inversely proportional to the degree of surface perfection and cleanliness. There is scope for further studies of surface crystallization of glasses with well characterized surfaces to determine the active contamination centers and the actual surface nucleation rates. A quantitative evaluation of the Turnbull ratio would be most enlightening.

I deeply thank my students and colleges, the ICG, and the financial support of CNPq, PADCT, FAPESP, CAPES and RHAÉ.

## REFERENCES

- [1] D. Uhlmann, J. Zarzycki, S. Shoules and others- Discussions of the Faraday Society (1970)] 50, 220.
- [2] E.D. Zanotto, A.F.Craievich and P.F.James- J.Mat. Science 21(1986)3050.
- [3] E.D. Zanotto and P.F.James- Glastech. Ber. 56K(1983)794.
- [4] A.F.Craievich, E.D.Zanotto and P.F.James- Bull. Soc. Franc. Min. Crist. 106(1983)169.
- [5] E.D.Zanotto and P.F.James- J.Non-Cryst. Solids 74(1985)373.
- [6] P.F.James, B. Scott and P. Armstrong-Phys. Chem. Glasses, 19 (1978)24.
- [7] K.F.Kelton- Sol. State Phys., 45(1991)75.
- [8] M.C.Weinberg and E.D.Zanotto- J. Non-Cryst. Solids 108(1989)99.
- [9] E.D.Zanotto- Proc. 34 Brazilian Congress Cer., v.2(1990)625.
- [10] S.Manrich and E.D.Zanotto- Ceramica (1993) submitted.
- [11] M.C.Weinberg; E.D.Zanotto and S.Manrich- Phys. Chem. Glasses, 32(1992)99.
- [12] P.F.James- J. Non-Cryst. Solids, 73(1985)517.
- [13] E.D.Zanotto- J. Non-Cryst. Solids, 89(1987)361.
- [14] E.D.Zanotto and M.C.Weinberg, Phys. Chem. Glasses, 30(1989)186.
- [15] E.Muller, K.Heide and E.D.Zanotto- J. Non-Cryst. Solids, 155(1993)56.
- [16] E.D.Zanotto and E.Muller- J. Non-Cryst. Solids, 130(1991)220.
- [17] R.Muller- PhD Thesis- University of Berlin (1989).
- [18] E.D.Zanotto- J. Non-Cryst. Solids, 129(1991)183.
- [19] A.M.Kalinina, N.S.Yuritsin, V.M.Fokin and V.N.Filipovich- Proc. Nat. Conf. Vitreous State, Leningrad (1990)235.
- [20] E.D.Zanotto- in Nucleation and Crystallization in Glasses and Liquids. Amer. Ceram. Soc. (1993)65.