NUCLEATION IN OXIDE GLASSES, METALS AND POLYMERS: ADVANCES IN THE LAST DECADE

Edgar Dutra Zanotto
Professor of Materials Enginnering
DEPARTMENT OF MATERIALS ENGINEERING
FEDERAL UNIVERSITY OF SÃO CARLOS
13565-905, São Carlos, SP- Brazil

This paper reviews two particular aspects of crystal nucleation in supercooled liquids: i) the validity of the classical nucleation theory for oxide, metallic and polymer liquids and ii) some remarkable trends observed on homogeneous and heterogeneous nucleation in oxide glasses.

INTRODUCTION

The knowledge of crystal nucleation and growth in supercooled liquids has tremendous scientific and technological importance. From a fundamental point of view, vitreous substances only exist when crystallization (the thermodynamically favoured path) can be suppressed during synthesis. From a technological perspective, there is a plethora of important commercial materials (glass-ceramics, semi-crystalline polymers, nano-alloys, etc) which are produced by controlled crystallization of supercooled liquids.

This article summarizes the applicability of the classical nucleation theory to the crystallization of oxide, metallic and polymer liquids as well as some remarkable trends observed on homogeneous and heterogeneous nucleation in oxide glasses. It does not review the relevant theories nor the experimental procedures due to space limitations. Here instead, solely a minimum of relevant equations, necessary to follow the article are presented.

1. THE VALIDITY OF CLASSICAL NUCLEATION THEORY (CNT)
1a) Supercooled Metals:

The pioneering work on nucleation in liquids date back from Fahrenheit in 1714 [1] who was able to supercool boiled water overnight at 15°F! Volmer & Weber and Becker & Döring came up with a theory of nucleation of liquids from the vapor phase in the early 30s. Turbull and Fischer [2] adapted that theory for the nucleation of solids from the liquid phase in 1949. This theory (CNT) has been the matter of intense debate, but nevertheless it is used up to now!

The first attempts to observe homogeneous nucleation were based on the so called "droplet technique" proposed by Vonnegut in 1948 [3] and perfected by Turnbull, Perepezko and others. In this case, one divides the liquid into a myriad of micron size droplets hoping that some of them will be free of nucleating impurities and thus homonucleation can be realized. The first experiments were carried out with liquids metals. In that case the maximum undercooling (before crystallization occurred) was measured and by making some assumptions on the minimum nucleation and growth rates, the surface energy (the unknown parameter in the nucleation equation) was estimated. Figure 1 shows an updated plot of surface energies calculated from undercooling data of elemental liquids.
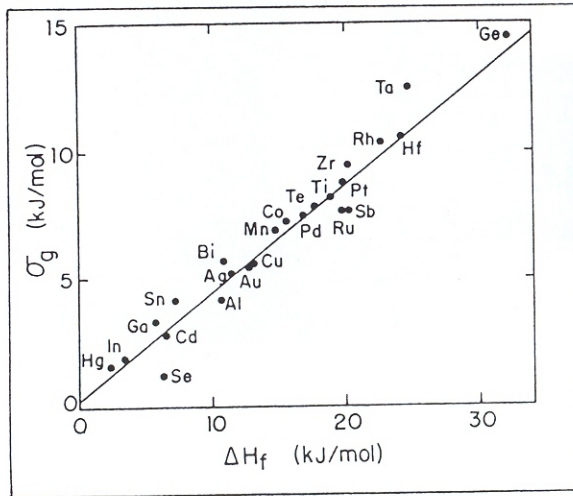

Figure 1. Molar interfacial energy ($\sigma N_A^{1/3} V_m^{2/3}$), derived from maximum undercooling of elemental liquids, as a function of molar heat of fusion, ΔH_f [4].

The slope of the curve in Figure 1, gives the average reduced surface energy, $\alpha = 0.43$ ($0.4 < \alpha < 0.5$), according to the expression:

$$\sigma = \alpha \cdot \Delta H_f / N_A^{1/3} \cdot V_m^{2/3} \qquad (1)$$

where V_m is the molar volume and N_A Avogadro's number.

Direct measurements of homogeneous nucleation rates I in

undercooled metals are very difficult due to the low liquid viscosity and extremely high crystal growth rates. Thus it is often assumed that one nucleation event is sufficient to trigger full crystallization. One of the few (indirect) measurements, where the number fraction of droplets which crystallize at each temperature was related to I, assuming fast crystal growth, was performed by Turnbull for Hg [5], and is shown in Figure 2. It is seen that I increases by a factor of ten in the narrow range of measurements (~ 1 degree K).
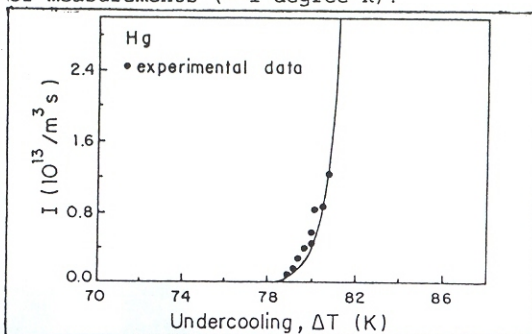

Figure 2. Homogeneous nucleation rates in liquid mercury [5].

In order to analyze nucleation data it is generally assumed that the molecular rearrangements at the nuclei/liquid interfaces are controlled by viscous flow, and thus, the transport term can be calculated using the Stokes-Einstein equation. Additionally, the interfacial energy σ is 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 [4]:

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

where A is a weakly temperature dependent term, η the viscosity, ΔG the thermodynamic driving force and K a geometrical constant. Thus, $Ln(I\eta/T)$ versus $1/(T.\Delta G^2)$ plots should be straight lines with A and σ_0 given by the intercept and slope, respectively.

In the analyses of nucleation in liquid metals, however, the whole pre-exponential term is considered constant since η does not depend much on temperature and the linear dependence of T is much weaker than the temperature dependent exponential term. Thus, the data of Figure 2 are shown, within the framework of Eq.(2), in Figure 3. A straight line results however, it gives an extrapolated pre-exponential factor 7 orders of magnitude higher than the theoretical value. In this case the thermodynamic driving force was approximated by $\Delta G=\Delta H_f.\Delta T/T_f$, the Turnbull approximation, valid for small undercoolings. In ligth of the numerous experimental difficulties (indirect estimates of nucleation rates in a narrow T range) and approximations in the analysis this discrepancy cannot be viewed as definitive. Turnbull suggested that the discrepancy could be eliminated by force fitting a positive temperature dependence for the surface energy σ.

With the discovery of glassy metallic alloys in the seventies, several researchers have tried to measure homogeneous nucleation rates

directly by microscopy methods. Some of most representative results were obtained by Tiwary et al.[6] and Morris [7] for a $Fe_{40}Ni_{40}P_{14}B_6$ alloy, which transforms by an eutectic mechanism. In this case the viscosities are highly temperature dependent and should be taken into account in the analyses of nucleation rates. Figure 4 shows a plot of $log(I\eta)$ versus $1/T\Delta G^2$, with $\Delta G=\Delta Hr.\Delta T(7T/Tr+6T)/Tr$, a expression believed to be more accurate than the Turnbull approximation for metallic glasses [4].

In contradiction with CNT, the curve is linear only above the maximum. Fitting the linear portion gives a pre-exponential factor 20 orders of magnitude **larger** than the theoretical value. Taking into account the complications associated with eutectic (non polymorphic) crystallization and the highly curved experimental plot, this was hardly a rigorous test of CNT. The discrepancy between the pre-exponentials, however, could be removed by force fitting a temperature dependent surface energy to the straight part of the plot [4].
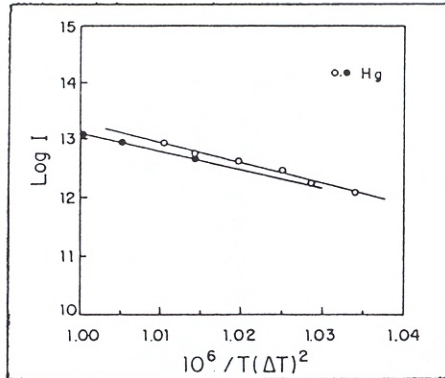

Figure 3. Logarithm of the steady-state nucleation rates as a function of undercooling for liquid Hg. Data from [5].
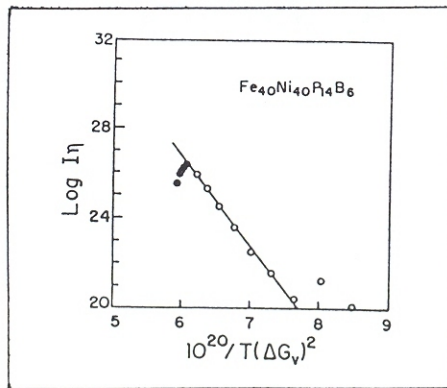

Figure 4. Log of nucleation rate x viscosity as a function of volume free energy a metallic glass. Data from (●) [6] and (○) [7].

1b) Polymers:

The distinguished feature of (flexible chain) polymer crystallization is the lammelar shape of the crystals, where the lateral dimensions, associated to a surface energy σ, are about 1000 times larger than the crystal thickness, l, associated to, an often called fold surface energy, σ_e.

An important fact about polymer crystallization is that the two surface energies can be obtained independently in a number of ways, by thermodynamic arguments as well as by kinetic experiments, ie. by a combination of nucleation and crystal growth measurements. The thermodynamic determination of σ_e comes from the fact that the lamella thickness, l, depend mainly on the crystallization temperature (lamellar ticknning is much slower than lateral growth), according to the following equation:

$$T_m(l) = T_m^{\circ}[1- 2\sigma_e/(\Delta H_f.l)] \tag{3}$$

where $T_m(l)$ and T_m° are the melting temperature of a crystal of thickness l and of a macroscopic crystal, respectively, and ΔH_f is the heat of fusion. Hence, one can estimate σ_e from the slope of a plot of T_m (measured by DSC) versus 1/l (measured by SAXS) of specimens crystallized in a range of temperatures. T_m° is given by the y-axis intercept in such plot.

The nucleation equation (2) can, in principle, be applied to polymers if σ_o^3 is replaced by $\sigma^2.\sigma_e$. Thus the product of the two surface energies can be derived from a plot of $Ln(I\eta/T)$ versus $1/(T.\Delta G^2)$. As in the case of metals, very few quantitative determinations of homogeneous nucleation rates have been published for polymers. The most typical example is Polyethylene, which has been studied by Cormia et al. [8], Gornick et al. [9] and Hoffmann et al. [10].

The droplet technique was utilized in [9] to estimate the isothermal nucleation rates of unfractionated linear polyethylene having a wide range of molecular weights. The half-times for the crystallization of droplets remaining unfrozen after cooling to the desired temperature, $\tau_{1/2}$, were related to the nucleation rate by the equation $I= \ln2/v.\tau_{1/2}$, where v is the droplet volume. Figure 5 shows A plot of half-time, corrected by the viscosity variation (using the Williams-Landel-Ferri empirical expression) as a function of $1/T.\Delta G^2$, in a 3°C temperature range. In this case, ΔG was calculated by the Hoffmann expression, taught to be accurate for polyethylene [10].

Table I shows the values of fold surface energy calculated by Hoffmann et al. [10] using data of several sources, including the above described results.

The fold surface energies, σ_e, calculated by methods 1, 2 and 3 assumed a value of 0.0146 J/m^2 for the lateral surface energy, σ, obtained from nucleation experiments on n-octadecane (σ is the work required to create a unit area of new lateral surface on the crystal from an equal amount of material from the interior of the crystal). Note that when σ_e is calculated from strictly kinetic measurements (method 4) a value of ~ 0.089 J/m^2 is found, in good agreement with the thermodynamic value of ~ 0.093 ($\pm$0.008)J/m^2. The other two methods of

analyses, from growth rate measurements (method 2) and from homogeneous nucleation measurements (method 3-from Fig. 5) also yielded very similar values, vindicating the assumption of homogeneous nucleation in this polymer.

Table I. Surface energies of polyethylene from kinetic and thermodynamic experiments.

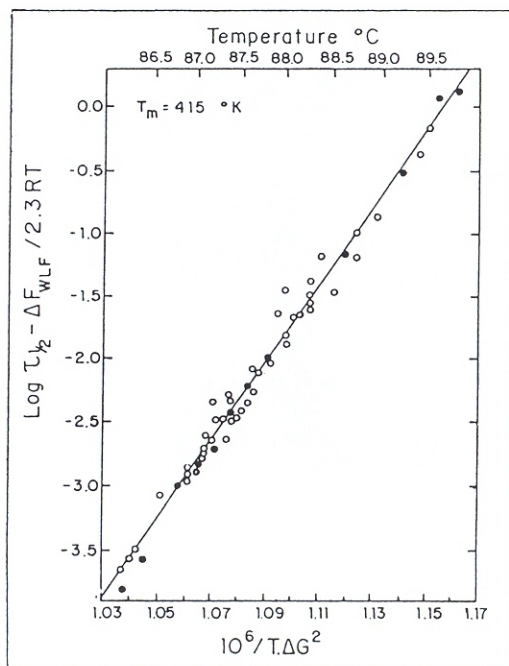| Method	σ_e (J/m^2)	σ (J/m^2)	T($^\circ$C)
1. Thermodynamic	0.093		>130
2. Growth $(\sigma_e.\sigma^2)$	0.088-0.095		~125
3. Nucleation $(\sigma_e.\sigma^2)$	0.089-0.092		~ 88
4. Nucleation $(\sigma_e.\sigma^2)$ + Growth $(\sigma_e.\sigma)$	0.089	0.0147	88-125

Figure 5 Half-time plot of isothermal nucleation of polypropylene. (o) sample of [8], (•) results of [9].

In spite of the impressive agreement between the several values of surface energy, the pre-exponential constant from Fig. 5 was found to be 12 orders of magnitude **higher** than the theoretical value. As for the other materials, this discrepancy could be removed by force fitting temperature dependent surface energies.

A similar study for undercooled water yielded a pre-exponential factor 11 orders of magnitude too large [11]. The only case where a negative disagreement of 4-5 om ($A_{exp} < A_{th}$) was found is for n-alcane liquids [11].

1c) Oxide Glasses:

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 $Li_2O.2SiO_2$ and $Na_2O-CaO-SiO_2$ glasses in **wide** temperature ranges (50-100 °C); and by Uhlmann and co-workers using indirect estimates (via crystal growth rates and overall crystallization) in $Na_2O.2SiO_2$ and $CaO.Al_2O_3.2SiO_2$ glasses (see [12]).

At that time there was an intense dispute; a team of authors defended the validity of CNT 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 ΔG, 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. [13] 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, $T_{max}/T_m \sim 0.55$, which were comparable to the maximum undercooling ever obtained for a pure element, Ga, in droplet experiments [4]. 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 $Li_2O.2SiO_2$ glass (from the same melt) having a known amount of H_2O and impurities, and retest CNT. We also performed similar experiments with a $BaO.2SiO_2$ glass, because this composition had not been properly analyzed before [12].

All studies previously described assumed that the molecular rearrangements at the nuclei/matrix interfaces were controlled by viscous flow. Thus, $Ln(I\eta/T)$ versus $1/(T.\Delta G^2)$ plots were constructed. 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 ΔG (even with absurd values of ΔG!). The only way to force agreement was by fitting a

weakly (positive) temperature dependent σ. 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 surface energy.

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 σ_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, α (molar interfacial energy / molar heat of fusion) has been obtained from fitting the experimental nucleation rates of a number of oxide 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, shown in Figure 1, $0.4 < \alpha < 0.5$ (which are probably slightly underestimated). Unfortunately, however, α is the unknown parameter of CNT, and has not been independently measured in glasses so far. Therefore, one can use this range of α to estimate the temperature dependence (but not the magnitude) of nucleation rates in undercooled liquids and glasses.

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 via the Stokes-Einstein equation to calculate the transport term of CNT and iii) the assumption that the surface energy is constant and equal to that of a macroscopic crystal, $\sigma = \sigma_0$. In other words, the nano-sized nuclei most probably have diffuse interfaces and the application on macroscopic concepts is doubtful.

Let us now discuss point i: Taken into account that σ comes out from fitting theory and experiment (from Eq. (2)), its value will not change if one finds that a metastable phase nucleates before the stable crystal. Additionally, the diffusion process in crystal nucleation is dictated mainly by atomic transport in the liquid (matrix) phase, and thus do not depend on the nature of the nucleating phase. Hence, we discarded possibility i) for the time being. We came to this conclusion because even using absurdly large or small values of ΔG (possible associated with the precipitation of metastable phases) would not bring theory and experimental data into accord.

We decided then 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:

$$I = (A'/\tau) \, \exp(-K \, \sigma_0^3 \, / T . \, \Delta G^2) \tag{4}$$

where τ is the temperature dependent induction period and the other parameters were defined before. Thus, one can fit the independently measured values of I, τ and ΔG to Equation (4) to obtain A' and σ_0 [14].
This type of calculation was performed for a number of glasses

[14], however, the temperature dependence and magnitudes were not well described by Equation (4). The disagreement was even worse than for the previous tests, using the viscosity (Figures 6 and 7).
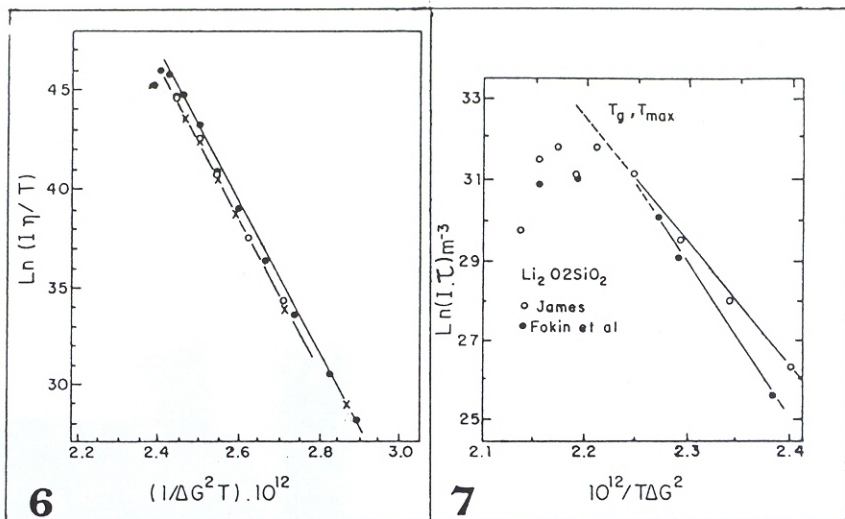

Figure 6. Nucleation plots for Li2O.2SiO2 glasses according to Equation (2). Nucleation data from different authors (●,○, x) described in [12]. SI units are employed.

Figure 7. Nucleation plots for Li2O.2SiO2 according to Equation (4). Steady-state nucleation rates, I, and induction times, τ, from James and Fokin et al., described in [14].

The third possibility is to assume a size or temperature dependent surface energy. In three occasions [15-17] we took Tolman's equation for $\sigma(r)$ and rederived CNT with this different view. Tolman's equation reads:

$$\sigma(r) = \sigma_0 \ / \ (1+ \lambda/r) \qquad (5)$$

where λ has the order of a molecular distance. Equation (5) is valid for $\lambda <<$ and overestimates the surface tension by 8% 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 (2) and (4) and were described in [15-17]. The problem now is the additional unknown parameter, λ. One may reasonably assume that λ 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) [15]. However, one may, instead, leave λ to be adjusted by force fitting CD-CNT to agree with both the magnitude and temperature of maximum experimental nucleation rate (CD2) [16-17].

Figure 8 shows the experimental and theoretical nucleation rates of $Li_2O.2SiO_2$ 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.
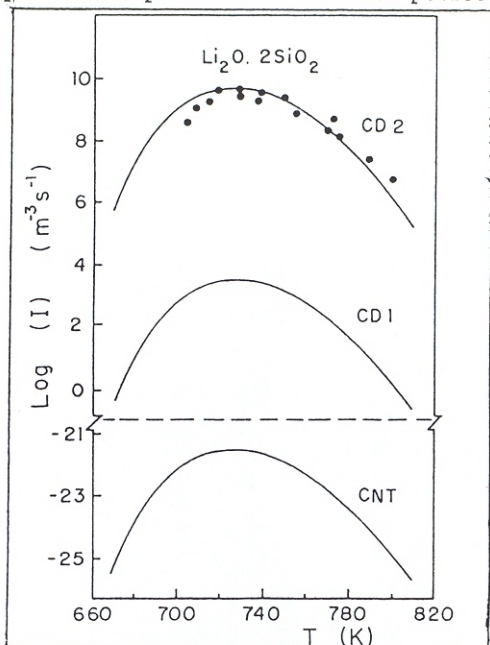

Figure 8. Crystal nucleation rate curves of $Li_2O.2SiO_2$ calculated by CNT, CD1 and CD2. Experimental data of James (●). Calculations of [16].

Table II summarizes the values of reduced surface energy, α, surface energy, σ, and discrepancy at T_{max} [$\log(I_{exp}/I_{th})$], for six silicate glasses calculated by Manrich and Zanotto [16].

Table II. Reduced surface energy, α, surface energy σ and discrepancy, $\log(I_{exp}/I_{th})$, for six silicate glasses [16].

	α	$\sigma (J/m^2)$	$\log(I_{exp}/I_{th})$
CNT	0.41-0.64	0.14-0.31	20-55
CD1	0.44-0.68	0.16-0.34	00-13
CD2	0.54-0.80	0.20-0.44	-----

Figure 9 shows the variation of σ 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 σ obtained by forcing both the temperature and magnitude of maximum

nucleation rate given by CD-CNT to agree with experiment. The size dependence of σ was transformed into temperature dependence. The interesting conclusion is that both methods show a moderate increase in σ with temperature, as found for undercooled metals and polymers. The challenge now is to devise a way to **measure** σ at a sufficiently high temperature, where the critical nucleus size is large enough. One possible way, is to find a glass whose crystal growth mechanism is via **2-D secondary nucleation**, to determine σ 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.
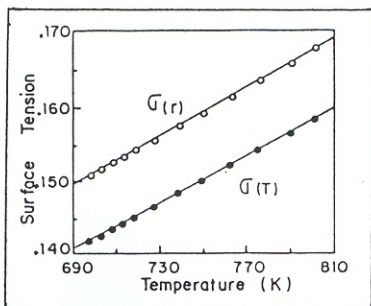

Figure 9. Temperature dependence of surface tension, σ, used by James to fit CNT to the nucleation data of Figure 8, and effective temperature dependence of σ found using a radius dependent surface tension, CD2 [17].

Conclusion

CNT is not capable of quantitatively predicting homogeneous nucleation rates in metals, polymers and glasses when a constant surface energy is used. It works much better (but still not perfectly) when a size and/or temperature dependent σ is taken into account. However, since this parameter cannot be evaluated independently, a main uncertainty still exists concerning the validity of CNT.

2. 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). Additionally, 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?

Following a hunch given by James [18], we collected literature data and reported some **trends** observed in the experimental nucleation behavior of stoichiometric oxide glasses [19, 20]. These glasses could be divided in two classes: Compositions having low reduced glass transition temperatures ($T_g/T_m < 0.6$) and whose temperatures of maximum nucleation rates, T_{max}, lye in the vicinity of T_g (DTA T_g) shows homo-

nucleation. 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 α and ΔG) occurs well bellow the glass transition range. Figure 10 exemplifies the trend, and allows one to distinguish 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 [20], but some data has been omitted for clarity.
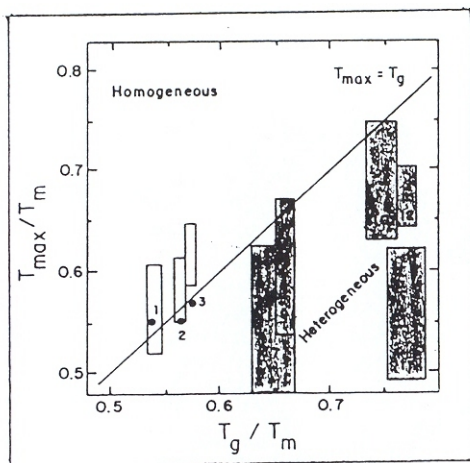

Figure 10. Calculated values of reduced temperature of maximum nucleation frequency against reduced glass transition temperature interval. (•) Experimental data.

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 bellow 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.

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 [21] 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** (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 [22]. 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 (σ) is sufficiently small as to make the nucleation rates measurable at sufficiently low temperatures, 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 σ large and move the nucleation curve to higher undercoolings, bellow T_g, where long induction times and, probably, low nucleation rates render the experimental detection of nucleation unfeasible.

REFERENCES

[1]   D.B.Fahrenheit, Phil. Trans. Roy. Soc. 39(1714)78.
[2]   D.Turnbull and J.C.Fischer, J. Chem. Phys.17(1949)71.
[3]   B.Vonnegut, J.Colloid Sci. 3(1948)563.
[4]   K.F.Kelton- Sol. State Phys., 45(1991)75.
[5]   D.Turnbull, J.Appl.Phys. 21(1950)1022.
[6]   R.S.Tiwary, J.C.Klaus and M.V.Heimendahl, Mater. Sci. Eng. 55(1982)1.
[7]   D.G.Morris, Acta Metall. 29(1981)1213.
[8]   R.L.Cormia, F.P.Price and D.Turbull, J.Chem.Phys., 37(1962)1333.
[9]   F.Gornick, G.S.Ross and L.J.Frolen, J. Polym. Sci: part C 18(1967)79.
[10] J.D. Hoffman, G.T.Davies and J.I. Lauritzen, Jr., Treatise on Solid State Chemistry, N.B. Hannay.-Plenun Press, NY 3(1976)ch.7.
[11] G.R.Wood and A.G.Walton, J.Appl.Phys. 41(1970)3027.
[12] E.D.Zanotto and P.F.James- J.Non-Cryst. Solids 74(1985)373.
[13] P.F.James, B. Scott and P. Armstrong-Phys. Chem. Glasses, 19(1978)24.
[14] M.C.Weinberg and E.D.Zanotto- J. Non-Cryst. Solids 108(1989)99.
[15] E.D.Zanotto- Proc. 34th Brazilian Congress Cer., v.2(1990)625.
[16] S.Manrich and E.D.Zanotto- Ceramica (1994) submitted.
[17] M.C.Weinberg; E.D.Zanotto and S.Manrich- Phys. Chem. Glasses, 32(1992)99.
[18] P.F.James- J. Non-Cryst. Solids, 73(1985)517.
[19] E.D.Zanotto- J. Non-Cryst. Solids, 89(1987)361.
[20] E.D.Zanotto and M.C.Weinberg, Phys. Chem. Glasses, 30(1989)186.
[21] E.Muller, K.Heide and E.D.Zanotto- J. Non-Cryst. Solids, 155(1993)56.
[22] E.D.Zanotto and E.Muller- J. Non-Cryst. Solids, 130(1991)220.