ISOTHERMAL AND ADIABATIC NUCLEATION IN GLASS

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A summary of both classical (isothermal) and adiabatic theories of nucleation is presented. Using experimentally determined parameters, such as viscosity, specific heat, glass transition temperature (T_g), melting temperature (T_f) and heat of fusion, the temperatures of maximum crystal nucleation rates, T_{max}, were calculated for several glass forming systems and compared with experimental data. It is shown that both theories give a good estimate for T_{max}. For systems which do not show volume (homogeneous) nucleation, T_{max} is lower than T_g. For systems which show volume nucleation, $T_{max} > T_g$. It is concluded that both theories can be used to predict the occurrence of internal crystal nucleation in glasses and that, in general, a high value of T_g $(T_g/T_f > 0.58)$ indicates the absence of internal nucleation.

1. Introduction

Crystal nucleation in glasses is of considerable scientific and technological importance. Of special interest is glass formation, which depends on the absence of nucleation during cooling from the molten state. For most systems, the presence of catalysts, container walls and "free" surfaces very often leads to heterogeneous nucleation and impairs glass formation. However, for a few systems (Li_2O-SiO_2, $BaO-SiO_2$, Na_2O-SiO, $CaO-SiO_2$, $Na_2O-CaO-SiO_2$ and $Al_2O_3-SiO_2$) volume nucleation has been reported to occur without the aid of catalysts. There is strong evidence that, in these cases, nucleation is homogeneous. Recently, James [1] demonstrated that for seven compositions within these systems the *experimental* values for T_{max}/T_f, where T_{max} is the temperature of maximum nucleation and T_f is the melting point, were all in the range 0.54 to 0.59. T_{max} was always at, or somewhat above T_g. He concluded that this remarkably consistent pattern of the results indicated that the observed nucleation is predominantly homogeneous. The question now arises: why does homogeneous nucleation occur in so few systems?

The objectives of this paper are threefold: (i) to answer the above question; (ii) to test how well the classical theory of Turnbull and Fischer [2] can predict the temperature of the maximum nucleation rate T_{max}; (iii) to test how well the new adiabatic theory of Meyer [3] can predict T_{max}.

2. Summary of the theories

2.1. Classical theory

Turnbull and Fischer [2] have applied the theory of Becker and Doring to the liquid → solid transition using the absolute reaction rates theory, and arrived at the following expression for the nucleation frequency I:

$$I = A \exp\left[-(\Delta G_D + W^*)/kT\right],\tag{1}$$

where ΔG_D and W^* are the kinetic and thermodynamic free energy barriers for nucleation, k is Boltzmann's constant and T the absolute temperature. The pre-exponential factor A can be expressed as

$$A = 2NV^{1/3}(kT/h)(\sigma/kT)^{1/2},\tag{2}$$

where N is the number of molecules of the nucleating phase per unit volume of liquid, V the molecular volume, σ the interfacial free energy per unit area and h is Plank's constant.

In the derivation of eq. (1) several assumptions were made, for instance: nuclei form isothermally by heterophase fluctuations, the equilibrium concentration of embryos is given by a Boltzmann type expression and σ does not depend on the radius of the nucleus or on temperature ($\sigma = \sigma_\infty$). Other simplifications were necessary for solving some mathematical expressions, and most of them were good for all but the smallest nuclei.

For a comparison with the experimental data for supercooled liquids, another assumption usually made is that the kinetic barrier, ΔG_D, is similar to that for viscous flow ΔG_η. Therefore, the molecular rearrangement for nucleation is related to viscous flow by means of the Stokes–Einstein equation to give

$$I = \frac{NkT}{2\pi a\lambda^2\eta} \exp(-W^*/kT),\tag{3}$$

where λ is the jump distance for an atom or molecule, "a" is the molecular diameter and η the viscosity coefficient. In eq. (3), the value of $2V^{1/3}$ $(\sigma/kT)^{1/2}$ is taken as unity for most nucleation problems of interest.

2.2. Adiabatic nucleation

Recently, a new theory was developed by Meyer [3] assuming that nucleation was an adiabatic phenomenon. Other assumptions were: (i) $c_p = (c_p^l + c_p^s)/2 =$ constant, where c_p^l and c_p^s are the molar specific heats of the liquid and solid phases at the melting point and therefore, c_p is the average specific heat; (ii) the solid/liquid interfacial tension is size dependent and is given by Tolman's equation

$$\sigma_r/\sigma_\infty = (1 + 2\delta/r)^{-1},\tag{4}$$

where δ is roughly equal to half of the intermolecular distance, and r is the radius of the nucleus [4]; (iii) the melting enthalpy is size dependent; (iv) the number of molecules of the adiabatic nucleus is that of a Wigner–Seitz primitive cell determining group of molecules, N_W, i.e., 13 molecules for a fcc or hcp structure and 15 molecules for a bcc structure (a mean value being $N_W \simeq 14$); (v) ordinary statistical (temperature) fluctuations [5] are considered instead of isothermal heterophase fluctuations.

This theory gives the maximum supercooling temperature for liquids, T'_{14} (SI units)

$$\frac{T'_{14}}{T_f} \simeq \frac{\Delta S_f}{c_p}\left(1.67 - 1.28(c_p)^{-1/2}\right)^{-1}\left[\exp(\Delta S_f/c_p) - 1\right]^{-1}, \tag{5}$$

where ΔS_f is the entropy of melting and T_f the melting point of the crystal phase.

Eq. (5) was fully discussed by Meyer [3].

3. Analysis of literature data

3.1. The classical theory

For spherical nuclei the thermodynamic barrier can be written:

$$W^* = 16\pi\sigma^3 V_m^2/3\Delta G^2, \tag{6}$$

where V_m is the molar volume of the nucleating phase and ΔG the molar free energy difference between the liquid and crystal phases.

Two approximations can be used to estimate ΔG:

$$\Delta G = -\Delta H_f(T_f - T)/T_f \tag{7}$$

and

$$\Delta G = -\Delta H_f(T_f - T)\left(\frac{2T}{T_f + T}\right)/T_f, \tag{8}$$

where ΔH_f and T_f are the latent heat and temperature of melting respectively. Eq. (8) was derived by Thompson and Spaepen [6] and gives a lower bound for ΔG, while eq. (7) gives an upper bound. This was verified for alkali disilicates where experimental data for ΔG exist [7].

The interfacial energy between nucleus and matrix, σ, cannot be measured independently of nucleation experiments and one has to use the empirical equation of Turnbull [8]:

$$\sigma = \alpha \, \Delta H_f(\rho/M)^{2/3}N_0^{-1/3}, \tag{9}$$

where $0.42 < \alpha < 0.55$ is a constant for glasses (assuming that σ is a constant) [1], ρ the density of the crystal phase, M the molecular weight and N_0 is Avogadro's number. A similar equation was also derived theoretically by Skapski [9].

The combination of eqs. (3), (6), (7), (8) and (9) gives:

$$I = \frac{NkT}{2\pi a\lambda^2\eta} \exp\left(-\frac{16\pi \Delta H_f T_f^2 \alpha^3}{3RT(T_f - T)^2} \right)$$

(10)

and

$$I = \frac{NkT}{3\pi a\lambda^2\eta} \exp\left(-\frac{4\pi \Delta H_f T_f^2 (T_f + T)^2 \alpha^3}{3RT^3(T_f - T)^2} \right).$$

(11)

Using $\alpha = 0.42$ in eq. (11) and $\alpha = 0.55$ in eq. (10) we obtain upper and lower bounds for the temperature of maximum nucleation frequency T_{max}. Therefore, to calculate the I versus T curve for a given glass forming system, in order to obtain T_{max}, the following parameters are necessary: the temperature dependence of viscosity, the melting enthalpy of the crystal phase and the melting temperature.

3.2. The adiabatic theory

The classical (isothermal) nucleation theory gives the nucleation frequency as a function of temperature. A maximum is obtained (at T_{max}), even in the hypothetical case of materials with a low and constant viscosity. In contrast to this, in the adiabatic nucleation model, nucleation is considered to be an instability phenomenon, occurring near a well defined, purely thermodynamic stability limit, at $T'_{\mu 14}$ [3]. The nucleation probability is zero down to almost T'_{14}, from where $T'_{\mu 14}$ is attained by mean (rms) temperature fluctuations. The onset of nucleation and the nucleation frequency distribution are not given, due to the mathematical simplifications. The nucleation probability is relatively high at T'_{14} and has a strongly increasing tendency as the temperatures decreases. Therefore, T'_{14} can be identified as the approximate maximum supercooling temperature [3]. Assuming that the maximum supercooling temperature is close to the temperature of maximum nucleation rate, one can estimate T_{max} by means of T'_{14}. The calculation of T'_{14} is easier than T_{max} and subjected to fewer errors because one does not need to know the viscosity as a function of the temperature, the thermodynamic driving force and α. It is only necessary to have experimental values of heat of fusion, melting point and average specific heat at T_f.

4. Results

Fig. 1 shows that T'_{14}/T_f decreases, i.e. the relative maximum-supercooling increases for high values of melting entropy and low values of heat capacity.

Fig. 2 shows the calculated (classical) nucleation curves for the $Li_2O \cdot 2SiO_2$ and $BaO \cdot 2SiO_2$ systems using eqs. (10) and (11) with $\alpha = 0.55$ and 0.42
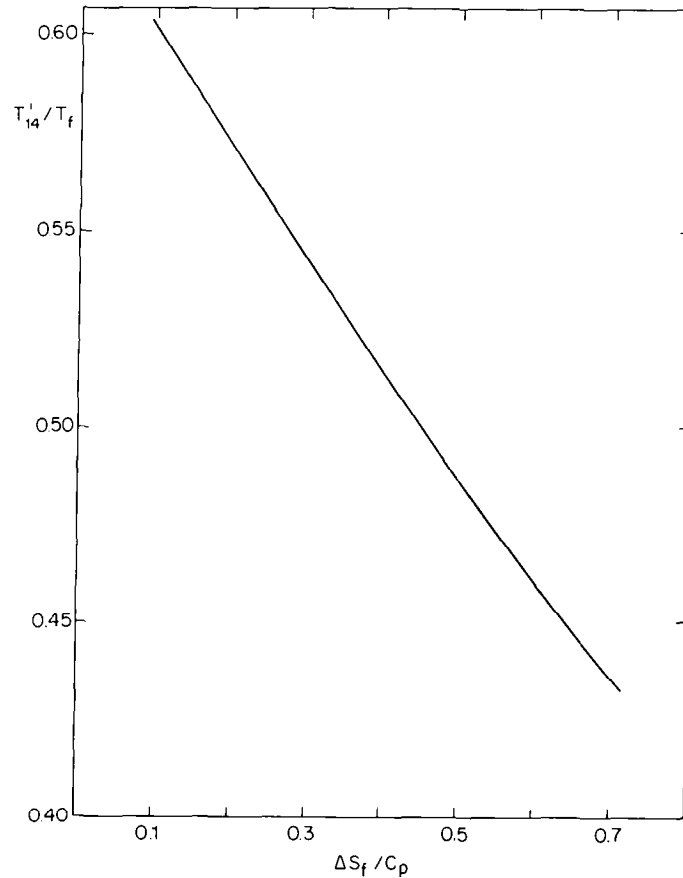
Fig. 1. Reduced maximum supercooling temperature as a function of melting entropy divided by specific heat. A value of $c_p = 50$ was assumed.

respectively. The experimental data of James [10,11] are also shown. It is clear that the classical theory underestimates the nucleation rates I by many orders of magnitude, in agreement with [11-14]. The temperature dependence of I, however, is well described by the classical theory if the correct values of ΔG and α are used [14]. Fig. 2 also confirms that eqs. (10) and (11) give lower and upper bounds for T_{max}.

Table 1 shows several parameters taken from the literature, see for instance [7,13-15], for 15 glass forming systems. It should be emphasized that some parameters such as T_g and viscosity, from which the Fulcher parameters are calculated, strongly depend on thermal history, presence of impurities and method of determination. Other parameters such as the melting temperature, heat of fusion and specific heat depend more on the accuracy of the experimental technique employed. The fact that most of these parameters were obtained by different authors, for different glasses and crystals, prepared
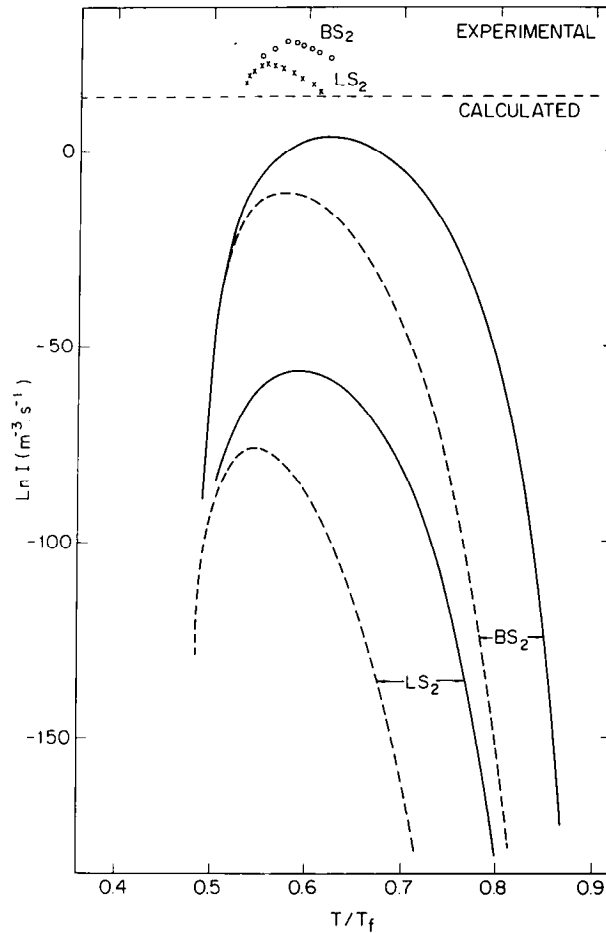
Fig. 2. Crystal nucleation rates versus reduced temperature for $Li_2O.2SiO_2$ $(LS)_2$ and $BaO.2SiO_2$ $(BS)_2$ glasses: (- - - - - -) calculated by eq. (10); (————) calculated by eq. (11).

under different conditions, makes the situation worse. Overall, one should expect viscosity and T_g to be the most unreliable of these data.

Table 2 shows the results for T_{max}/T_f (or T'_{14}/T_f) calculated by means of eqs. (10) and (11) (classical theory) and eq. (5) (adiabatic theory) for 15 glass forming systems. It should be emphasized that internal (homogeneous) nucleation has been observed in the first five systems: $Na_2O.SiO_2$ [16], $Li_2O.2SiO_2$ [13], $Na_2O.2CaO.3SiO_2$ [12], $CaO.SiO_2$ [17] and $BaO.2SiO_2$ [13]; and only surface (heterogeneous) nucleation has been reported to occur in the other systems of table 2.

The value of T_{max}/T_f (or T'_{14}/T_f) calculated by both classical and adiabatic theories are plotted as a function of the reduced glass transition temperatures in fig. 3. This figure also shows the line for $T_{max} = T_g$ (or $T'_{14} = T_g$).

Table 1

Literature data for thermodynamic parameters, T_g and viscosity for 15 glass forming systems

System	T_f(K)	DTA T_g(K)	ΔH_f (J/mol.)	C_p [c] (J/mol. K)	Fulcher Parameters A	B	T_0(K)
$Na_2O.SiO_2$	1362	733	26100	100	–	–	–
$Li_2O.2SiO_2$	1307	725	57300	243	1.81	1347	595
$Na_2O.2CaO.3SiO_2$	1564	852	87900	400	– 4.86	4893	547
$CaO.SiO_2$	1817	1030	56000	136	–	–	–
$BaO.2SiO_2$	1693	963	37000	240	1.83	1702	795
GeO_2	1387	819 [a]	15100	–	– 9.94	17962	0
$K_2O.2SiO_2$	1309	770	31800	84	–	–	–
$CaO.MgO.2SiO_2$	1664	1003	127500	364	–	–	–
$CaO.Al_2O_3.2SiO_2$	1826	1116 [a]	135500	376	– 5.85	6750	738
$Li_2O.P_2O_5$	926	586 [a]	61700	–	– 4.10	2000	462
$Na_2O.2SiO_2$	1147	740	35500	251	– 0.64	2315	541
$PbO.SiO_2$	1037	725	34000	171	[b]	[b]	[b]
$Na_2O.Al_2O_3.6SiO_2$	1380	966	55000	347	–	–	–
SiO_2	1996	1493	9600	79	– 13.51	37157	0
B_2O_3	723	553	22600	119	– 5.02	3665	333

[a] T_g obtained from viscosity curves ($\eta = 10^{12}$ Pa s).

[b] $\text{Log}\,\eta = 10.0 - 2.8 \times 10^4\ T^{-1} + 2.0 \times 10^7\ T^{-2}$ (Pa s).

[c] C_p values at the melting point.

Taking into account the many approximations of both theories and the uncertainties in the experimental parameters of table 1, it can be concluded

Table 2

Experimental and calculated values for T_{max}/T_f and T_{14}/T_f for 15 glass forming systems

System	T_g/T_f	Internal nucleation Adiabatic T'_{14}/T_f	Classical T_{max}/T_f	Experimental T_{max}/T_f
$Na_2O.SiO_2$	0.54	0.59	–	0.54
$Li_2O.2SiO_2$	0.55	0.58	0.54/0.59	0.55
$Na_2O.2CaO.3SiO_2$	0.55	0.58	0.50/0.58	0.55
$CaO.SiO_2$	0.57	0.57	–	0.58
$BaO.2SiO_2$	0.57	0.60	0.58/0.62	0.58
		Surface nucleation		
GeO_2	0.59	–	0.56/0.65	n.o. [a]
$K_2O.2SiO_2$	0.59	0.56	–	n.o.
$CaO.MgO.2SiO_2$	0.60	0.56	–	n.o.
$CaO.Al_2O_3.2SiO_2$	0.61	0.56	0.53/0.60	n.o.
$Li_2O.P_2O_5$	0.63	–	0.58/0.62	n.o.
$Na_2O.2SiO_2$	0.65	0.59	0.59/0.63	n.o.
$PbO.SiO_2$	0.67	0.58	0.50/0.59	n.o.
$Na_2O.Al_2O_3.6SiO_2$	0.70	0.59	–	n.o.
SiO_2	0.74	0.64	0.67/0.73	n.o.
B_2O_3	0.75	0.56	0.62/0.67	n.o.

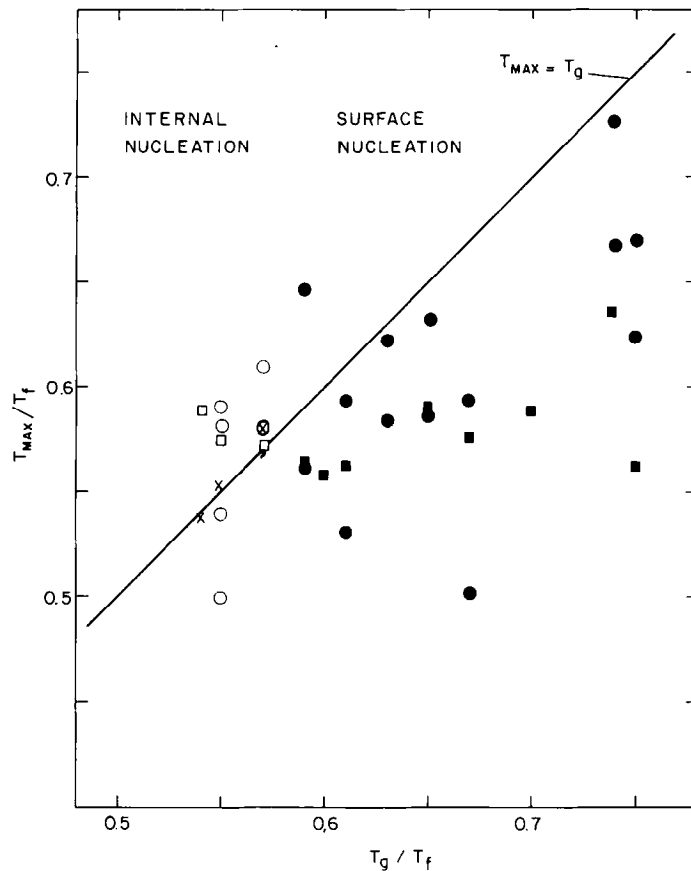[a] n.o. = internal nucleation has not been observed.

Fig. 3. Reduced temperature of highest nucleation frequency versus the reduced glass transition temperature: adiabatic theory: □, volume nucleation; ■, only surface nucleation. Classical theory – upper and lower bounds; ○, volume nucleation; ● only surface nucleation. Experimental results, ×.

that the values predicted by the theories are, surprisingly, in very good agreement. For glasses which crystallize internally, T'_{14} and $T_{max} > T_g$ and $0.54 < T_g/T_f < 0.58$; whereas for glasses which crystallize only from the surface, T'_{14} and $T_{max} < T_g$ and $T_g/T_f > 0.58$.

5. Discussion

Let us now try to answer the questions put forward in the introduction:

(i) Why is it that only a few systems present internal nucleation? This is because for such systems the ratio T_g/T_f is low (< 0.58) and the temperatures of highest nucleation frequency T_{max} or T'_{14} predicted by the theories, are

equal to or higher than T_g. Therefore, nucleation can occur in reasonable periods of time. The reason why T_g/T_f is low for these systems is related to the structure and relaxation kinectics of the liquid and should be pursued further.

For systems which crystallize only from the surface $T_g > T_{max}$ or T'_{14} and, therefore, volume nucleation cannot occur in reasonable times due to limited (slow) molecular rearrangement and long induction periods [10].

(ii) How well can the classical theory predict T_{max}? Table 2 and fig. 3 show that for glasses which crystallize internally, the predicted value for T_{max} agrees well with T'_{14} and also with the experimentally determined temperatures of the maximum nucleation rate. For glasses which crystallize from the surface the same behaviour is verified, i.e. T_{max} agrees well with T'_{14}. These findings confirm the conclusions of Zanotto and James [14] who found good agreement with the temperature dependence given by classical theory.

(iii) How well can the adiabatic theory predict T_{max}? The agreement of T'_{14} with the experimental values for T_{max} is excellent for the first five systems in table 2. The adiabatic theory also correctly predicts that T'_{14} is substantially lower than T_g for systems which do not crystallize internally. Meyer [3,18] has shown, in agreement with the present results, that his theory also predicts very well the maximum supercooling observed for small droplets of liquid metals such as Ga, P, Hg, Pb and Sn. Several polymers are being studied at the moment.

Finally, it should be stressed that much theoretical work has to be done to explain why both theories are in agreement despite their completely different assumptions and nature. Overall, we can say that values of T_{max} calculated by the classical theory depend on the values chosen for α, which were obtained by maintaining the interfacial energy constant and fitting the theory to the experimental nucleation data for $Li_2O.2SiO_2$, $BaO.2SiO_2$ and $Na_2O.2$ $CaO.3SiO_2$ [13,14]. If lower values were used for α ($\alpha = 0.3$), the individual values for T_{max} would increase but the overall pattern of results (fig. 3) and conclusions would not change. On the other hand, the values for T'_{14}, predicted by the adiabatic theory, do not depend on adjustable parameters and, therefore, this theory seems to be more predictive.

One should not overlook, however, that in spite of the excellent results, the adiabatic nucleation model is much less pretentious than the classical nucleation theory. The adiabatic nucleation model does not predict quantitative nucleation frequencies. It just indicates whether and where homogeneous nucleation occurs.

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