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CRITICAL COOLING RATE CALCULATIONS FOR GLASS FORMATION

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An assessment is made of the various factors which are involved in the calculation of critical cooling rates for glass formation. In particular, attention is focused upon the sensitivity of computed critical cooling rates R_c to various approximations and uncertainties in physical parameter data. SiO_2 and GeO_2 are chosen as model systems to illustrate the major features. It is shown that R_c is rather insensitive to the mode of computation of the volume fraction crystallized, but is quite dependent upon the material parameters which enter into the nucleation and crystal growth expressions.

1. Introduction

Kinetic approaches to glass formation have been used extensively to predict the glass-forming ability of metallic and inorganic glasses [1–5]. The key idea underlying this method is that all materials will form glasses if undercooled sufficiently rapidly to prevent crystallization. Hence, kinetic treatments focus on the computation of the crystallization rate for non-isothermal cooling paths, and the concomitant cooling rate required to avoid the formation of more than a specific volume fraction of crystals at the termination of cooling. The latter rate, termed the critical cooling rate for glass formation and denoted by R_c, is the central output of the theory. The critical volume fraction of crystals x_c is usually taken to be 10^{-6}.

The calculation of R_c involves three ingredients: (1) the selection of a model to compute the volume fraction crystallized for a non-isothermal process (given $I(T)$ and $u(T)$, i.e., the temperature dependent nucleation and growth rates); (2) the choice of the nucleation and growth expressions; and (3) the selection of the values of several parameters which enter into the nucleation and growth equations. Either for reasons of convenience or by necessity, significant approximations are often involved in the execution of one or all of the above three steps. Since these approximations could seriously affect the reliability of critical cooling rate predictions for glass formation, the sensitivity of R_c to these choices should be assessed.

Here, the influence of particular options for (1) and (3) upon the values of R_c are explored. In particular, an investigation is performed of the critical cooling rates to form glassy SiO_2 and GeO_2 and the dependence of R_c on both theoretical model and materials parameters.

2. Nucleation and growth expressions

For all calculations performed herein the classical, steady state, nucleation equation [6] is employed. Therefore,

$$I(T) = \frac{KT}{\eta} \exp\left(-K'\alpha^3/T[\Delta G]^2\right). \tag{1}$$

In eq. (1), T is the absolute temperature, η is the viscosity, ΔG is the bulk free energy difference between liquid and crystal, α is the Turnbull ratio [7], and K, K' are constants [8]. Several comments are warranted regarding the use of eq. (1). First, this equation does not account for transient

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nucleation effects [9]. Such effects are known to be of greater importance when the viscosity of the melt is large, and hence could be of significance for the systems studied here (i.e., SiO_2 and GeO_2). However, the primary aim of this work is to test the sensitivity of R_c to various approximations and not to make accurate predictions of critical cooling rates for SiO_2 and GeO_2. Further, the use of critical cooling rate calculations is of most interest with regard to marginal glass-forming systems, typified by small melt viscosities. Thus, for those systems where critical cooling rate calculations are of most significance, transient nucleation effects are likely to be unimportant. Next, the magnitude of the crystal nucleation rate as predicted by eq. (1) may be seriously in error [10,11]. However, the temperature dependence of $I(T)$ as given by eq. (1) is in agreement with the experiment, and thus the calculated values of R_c are at worst in error by the same constant scaling factor. Hence, eq. (1) can be reliably used to predict relative values of R_c, as well as for testing the sensitivity of R_c to various approximations.

For materials characterized by low values of the entropy of fusion ($\Delta S_f/R < 2$, where R is the gas constant), a normal growth mechanism may be assumed [12]. The corresponding growth equation is

$$u(t) = \frac{K''' T}{\eta}\left[1 - \exp\left(-\left|\frac{\Delta G}{RT}\right|\right)\right]. \qquad (2)$$

Since SiO_2 and GeO_2 have reduced entropies of fusion less than 2, eq. (2) applies for these two compositions.

If ΔC_p, the difference between the liquid and crystal specific heats, is taken as constant, then ΔG is given by

$$\Delta G = -T_m \, \Delta S_f \left[(1 - T_r)(1 - \gamma) - \gamma T_r \ln T_r\right]. \qquad (3)$$

In eq. (3), T_m is the melting temperature, $T_r = T/T_m$, and $\gamma = \Delta C_p/\Delta S_f$. Even if ΔC_p is temperature dependent, eq. (3) can be useful and informative since the temperature region over which significant crystallization occurs is usually quite narrow. Hence, ΔC_p is not expected to vary much in this small temperature regime and can be considered essentially constant here. Thus, ΔG can be

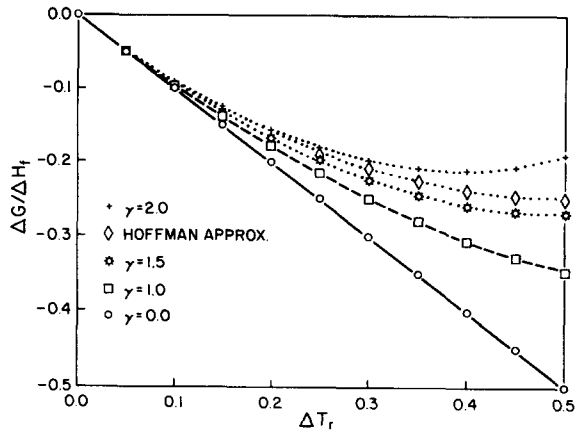

Fig. 1. Reduced bulk free energy difference between crystal and melt versus reduced undercooling for several values of gamma and the Hoffman Approximation.

described in terms of an 'effective' value of γ, characteristic of this temperature zone. Two common approximations for ΔG are the Hoffman approximation and the assumption that $\Delta C_p = 0$ (eqs. (4a, b) respectively):

$$\Delta G = -T_m \, \Delta S_f (1 - T_r) T_r \quad \text{(Hoffman)} \qquad (4a)$$

$$\Delta G = -T_m \, \Delta S_f (1 - T_r) \quad (\Delta C_p = 0). \qquad (4b)$$

The Hoffman approximation is quite close to the assumption that $\gamma = 1.5$, as illustrated in fig. 1. One observes from this figure, also, that all values for ΔG are quite similar for small undercoolings, but very significant differences result at small reduced temperatures. Thus, the error introduced in computing the crystallization rate due to uncertainties in ΔG will depend crucially upon the location of the maximum crystallization rate. If the temperature region of significant crystallization occurs for $\Delta T_r \lesssim 0.15$, then calculated R_c values will not be seriously affected by the choice of the model (or value of γ) for ΔG.

3. Phase transformation model

The volume fraction of the crystals formed may be found from the JMA equation [13,14]. If one assumes spherical growth, then the volume frac-

tion transformed at time t, $x(t)$ is

$$x(t) = 1 - \exp\left\{ -\frac{4\pi}{3} \int_{t_0}^{t} \mathrm{d}t' I(t') \left[\int_{t'}^{t} u(t'') \, \mathrm{d}t'' \right]^3 \right\}, \tag{5}$$

where t_0 is the initial time. If, further, one presumes that the nucleation and growth rates possess no intrinsic time dependence and that the cooling rate is constant, then it readily follows from eq. (5) that

$$R_{\mathrm{ce}} = \left\{ \frac{\frac{4\pi}{3} \int_{T_{\mathrm{m}}}^{T_{\mathrm{f}}} \mathrm{d}T I(T) \left[\int_{T}^{T_{\mathrm{f}}} u(T') \, \mathrm{d}T' \right]^3}{x_{\mathrm{c}}} \right\}^{1/4}, \tag{6}$$

where it was assumed that $T = T_{\mathrm{m}}$ at $t = t_0$ and the fact that $x_{\mathrm{c}} \ll 1$ was employed. T_{f} corresponds to the temperature at the termination of cooling. R_{ce} will be termed the exact critical cooling rate since no 'extra' assumptions are made in its derivation (i.e., only the weak assumptions stated above and those inherent in the derivation of the JMA equation).

A second, simpler but approximate method which has been used to calculate critical cooling rates relies on the use of TTT (time–temperature–transformation) diagrams [15]. As described below, this technique identifies the critical cooling curve as the one which intersects the nose of a TTT diagram (see fig. 2). The critical TTT diagram is described by

$$x_{\mathrm{c}} = (\pi/3) I(T) u^3(T) t^4. \tag{7}$$

The critical cooling rate is the slope of the straight line labelled CR shown in fig. 2. Therefore,

$$R_{\mathrm{cn}} = (T_{\mathrm{m}} - T_{\mathrm{n}})/t_{\mathrm{n}}, \tag{8}$$

where R_{cn} designates the critical cooling rate determined by the nose method, and T_{n}, t_{n} are the temperature and time at the nose, respectively. T_{n} can be determined by solving

$$\frac{\mathrm{d}}{\mathrm{d}T} \left(I(T) u^3(T) \right) = 0 \tag{9}$$

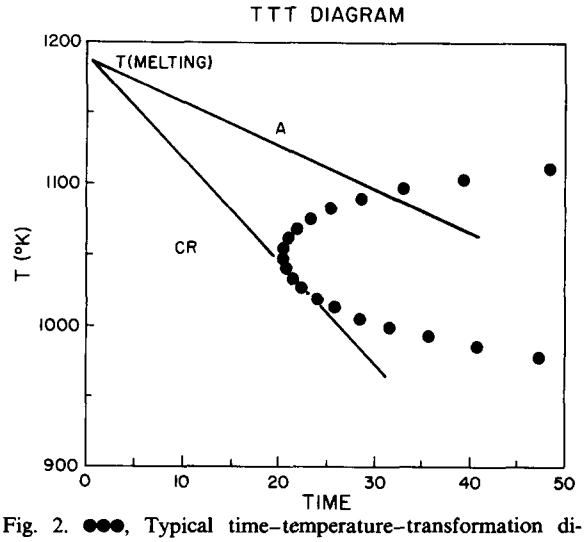

Fig. 2. ●●●, Typical time–temperature–transformation diagram. CR is critical cooling path and A is an arbitrary path with subcritical rate.

since it corresponds to the temperature of maximum crystallization rate. Combining eqs. (7) and (8) one obtains

$$R_{\mathrm{cn}} = \frac{(T_{\mathrm{m}} - T_{\mathrm{n}}) \left[(\pi/3) I(T_{\mathrm{n}}) u^3(T_{\mathrm{n}}) \right]^{1/4}}{x_{\mathrm{c}}^{1/4}}. \tag{10}$$

The required critical cooling rates to form SiO_2 and GeO_2 glasses were computed using the approximate TTT method and the exact method for several values of α and γ. The data that were employed for these calculations are shown in table 1, and the results are presented in table 2. We opted to present the ratios of the calculated rates since the main objective is to compare the outcome of the two methods. Also, the absolute values of the calculated rates may not be very meaningful due to the reasons discussed previously. It is observed that the nose method con-

Table 1
Physical parameters used for computation of R_{c}

Composition	T_{m} (K)	$\Delta S_{\mathrm{f}}/R$	$\log_{10}\eta = A + B/T$ (Pa s)	
			A	B
GeO_2	1387.0	1.31	−9.94	17962.0
SiO_2	1996.0	0.603	−6.884	27115.0

Table 2
Calculated critical cooling rate ratios for SiO_2 and GeO_2 [a)]

$\alpha =$	0.5	0.33	0.5	0.33
	R_{cn}/R_{ce} for GeO_2		R_{cn}/R_{ce} for SiO_2	
$\gamma = 0$	4.8	2.8	7.3	4.5
$= 1$	4.4	2.7	6.8	4.2

[a)] R_{cn} computed from eq. (10) and R_{ce} from eq. (6).

sistently overestimates R_c, but that critical cooling rates obtained via this procedure are well within an order of magnitude of the R_c values obtained using the exact theory.

4. Effects of material parameters

Next, the sensitivity of calculated values of R_c to changes in physical parameters is explored.

The Turnbull ratio α solely influences the nucleation rate. Inspection of eq. (1) shows that the larger the value of α, the smaller the magnitude of $I(T)$. Thus, one anticipates large values of α to tend to promote small R_c. Also, as α increases, the temperature of the maximum nucleation rate $I(T_{max})$ shifts to lower temperature. Since the temperature at which maximum crystal growth occurs is typically much higher than $I(T_{max})$, increasing α tends to reduce the overlap of the nucleation and growth curves. This feature produces a reduction in the crystallization rate during cooling, and hence also reduces R_c.

The relative change of the critical cooling rate as a function of α is shown for SiO_2 and GeO_2, respectively, in figs. 3 and 4. It is observed that the critical cooling rates for both compositions decreased by several orders of magnitude as α increases from $\frac{1}{3}$ to $\frac{1}{2}$. Since $I \sim \exp(-\alpha^3 F(T))$, it is not surprising that R_c is quite sensitive to small changes in α. Also, we have calculated the shift in the nose of the TTT diagrams as α is changed from $\frac{1}{3}$ to $\frac{1}{2}$. For silica there is a decrease of approximately 140 K of the nose temperature while, for GeO_2, T_n is lowered by about 115 K. As discussed above, this shift produces a decrease in the volume fraction crystallized during cooling, and hence also is a contributing factor to the smaller critical cooling rates computed.

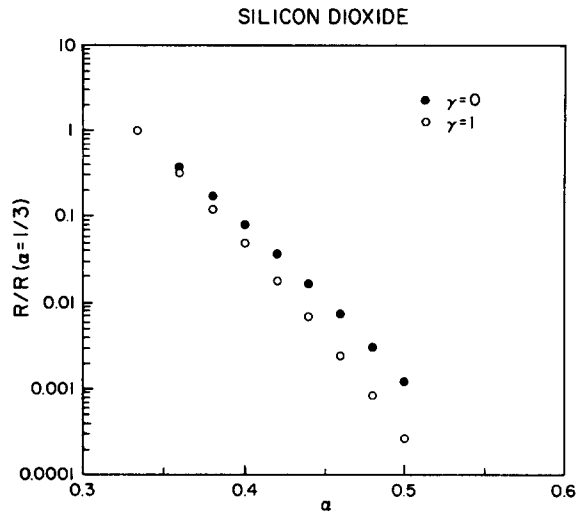

Fig. 3. Variation of reduced critical cooling rate for glass formation for SiO_2 versus α for $\gamma = 0$ and $\gamma = 1$.

In contrast to α, variations in γ affect both nucleation and growth rates. However, γ appears in the nucleation and growth expressions only through ΔG. Hence, in order to obtain a qualitative understanding of the effect of increasing γ upon the critical cooling rate one must ascertain: (1) the variation in $|\Delta G|$ as a function of γ, and (2) the concomitant change produced in R_c as

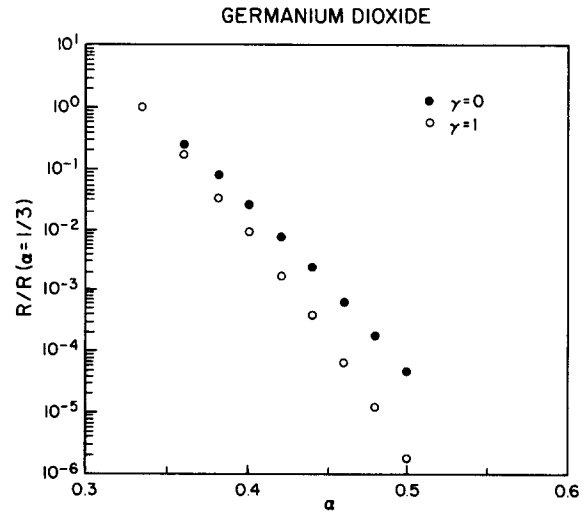

Fig. 4. Variation of reduced critical cooling rate for glass formation for GeO_2 versus α for $\gamma = 0$ and $\gamma = 1$.

$|\Delta G|$ is altered. Step 1 may be accomplished easily by recourse to inspection of fig. 1. Here, one may observe that at any given undercooling $|\Delta G|$ decreases as γ increases. Next, from inspection of eqs. (1) and (2), it is clear that both nucleation and growth rates decline in magnitude as $|\Delta G|$ becomes smaller. Thus, we may conclude that the critical cooling rates are expected to decrease as γ is increased. This anticipation is borne out by our results. In figs. 5 and 6, normalized critical cooling rates for SiO_2 and GeO_2, respectively, are plotted versus γ for $\alpha = \frac{1}{3}$ and $\alpha = \frac{1}{2}$. It is observed that R_c is a decreasing function of γ in all cases.

There are two striking features concerning these plots which merit discussion. First, one notes that the sensitivity of R_c to changes in γ is much larger when $\alpha = 0.5$ (especially in the case of GeO_2). Second, one finds that typically for variations in α and γ of equal magnitude, much larger differences in R_c result when α is changed. In order to understand the origins of these results, several additional findings must be mentioned. Calculations reveal that for fixed α the location of the nose temperature T_n is nearly invariant to all changes in γ. This result stems from the fact that while $I(T_n)$ and $u(T_n)$ vary significantly with γ, $I'(T_n)/I(T_n)$ and $u'(T_n)/u(T_n)$ (where the primes denote temperature derivatives) are nearly invariant. Also, one may assume that the largest contribution to the volume fraction crystallized occurs in the vicinity of T_n. Therefore, one can compute the temperatures (or reduced undercoolings) at which significant crystallization is expected to occur for the various cases (i.e., SiO_2 or GeO_2 for different values of α). This procedure has been carried out. For example, it is found that for SiO_2 when $\alpha = \frac{1}{3}$, ΔT_r at the nose is 0.17. Since the location of the maximum crystallization rate is virtually invariant to γ, one may fix $\Delta T_r = 0.17$ and appeal to fig. 1 in order to assess the changes in ΔG produced by changes in γ. One observes that at this undercooling ΔG is quite insensitive to γ, and hence R_c will be a weak function of γ. On the other hand for GeO_2, when $\alpha = 0.5$, the maximum crystallization rate occurs at $\Delta T_r = 0.3$. Figure 1 shows a significant difference between $|\Delta G|$ at $\gamma = 0$ and $\gamma = 2$ for this undercooling. Hence, the variation in R_c with γ for this case is substantial. Finally, it is observed that $|\Delta G|$ appears to the second power in the nucleation equation while α appears as the cube. Thus, the nucleation rate is anticipated to be more sensitive to changes in α then to those in $|\Delta G|$ (i.e., γ). Since changes in the magnitude of the crystallization rate at the nose appears to be influenced to a greater extent

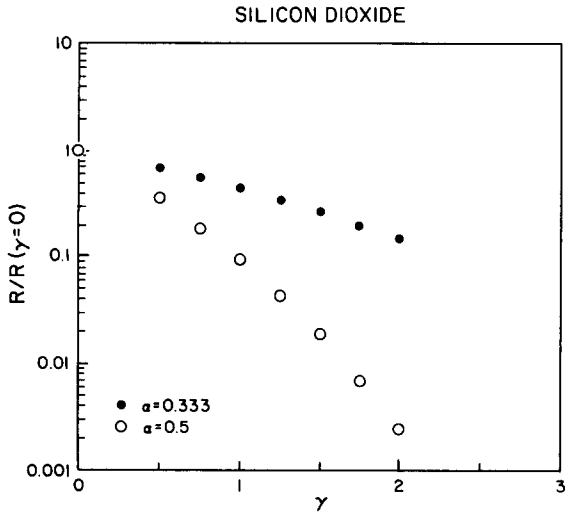

Fig. 5. Change in normalized critical cooling rate for glass formation for SiO_2 versus γ for $\alpha = \frac{1}{3}$ and $\alpha = \frac{1}{2}$.

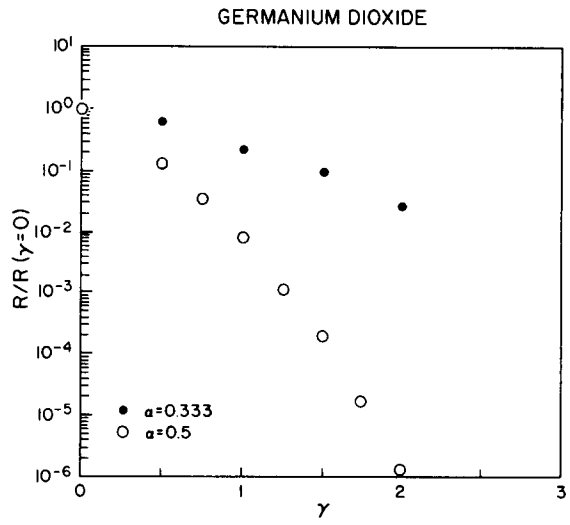

Fig. 6. Change in normalized critical cooling rate for glass formation for GeO_2 versus γ for $\alpha = \frac{1}{3}$ and $\alpha = \frac{1}{2}$.

(in this study) by variations in the nucleation rate at T_n, one concludes that variations in α will produce larger changes in R_c than equivalent size variations in γ.

5. Discussion

The results presented in table 2 indicate that the TTT method yields reasonable (order-of-magnitude) estimates of the critical cooling rate for glass formation. The method assumes that the crystallization kinetics are as rapid at temperatures above the nose of the TTT curve as at the nose and neglects crystallization at temperatures below the nose. Since the times at temperatures around the nose T_n (within tens of degrees Centigrade for typical oxide systems) should be most important, assuming that cooling must take place in the time of the nose over the full temperature range between T_m and T_n causes the TTT method to overestimate R_c. The relationship between the TTT (nose method) and the exact procedure for predicting critical cooling rates has been discussed in more detail elsewhere [16].

In a related study, two of the authors have shown that use of the additivity model overestimates R_c by less than an order of magnitude [17]. In the additivity model, the transformation rate dx/dt is a separable function of T and x [18]. It is only valid when the nucleation and growth curves substantially overlap or when site saturation occurs [17]. Despite the approximations used in the TTT and additivity models, values of the critical cooling rates calculated using these and the more precise JMA model all agree to within an order of magnitude.

On the other hand, it has been demonstrated that R_c is quite sensitive to variations in α and γ. It should be recalled that γ was introduced to account for the possible temperature dependence of ΔC_p. Precise specific heat measurements for crystal and melt would obviate the need for this parameter, and would remove one degree of uncertainty in critical cooling rate calculations. However, the situation with regard to α is more serious. The Turnbull ratio α is utilized to eliminate the liquid–crystal surface tension in favor of the enthalpy of fusion. However, the proportionality constant α is now known a priori, and must be determined from nucleation experiments. Also, the liquid–crystal surface tension is an unknown quantity, and must be obtained experimentally in a similar fashion. Independent determination of α (or surface tension) is thus highly desirable.

The strong sensitivity of R_c to variations in α and γ can be understood if one refers to eqs. (1)–(4). α influences the extent of crystallization (and hence R_c) in two manners. Since $I \propto \exp(-\alpha^3)$, smaller values of α produce larger nucleation rates at all temperatures and thus larger x. This tends to increase R_c. Also, for smaller α the nucleation curve shifts to higher temperatures producing a larger overlap of nucleation and growth curves. This feature also increases x (in cooling experiments), and thus R_c. Hence, both effects of decreasing α contribute to enhancing the magnitude of R_c. Increasingly higher values of γ decrease the thermodynamic driving force (fig. 1) which in turn leads to diminished magnitudes for I, U and consequently R_c.

The calculations presented in the present paper were carried out to illustrate the effect of theoretical models and material parameters on the critical cooling rate for glass formation. They were not intended to provide precise predictions for R_c, since such calculations would necessitate the use of accurate thermodynamic data, as well as the inclusions of other effects (such as transient nucleation). In fact, a primary purpose of this work was to assess the effect of the use of imprecise data on predicted critical cooling rate values. On the whole, it was found that R_c is strongly sensitive to changes in the input parameters investigated in this study, and is to a large degree insensitive to the theoretical model used.

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