SENSITIVITY OF CRITICAL COOLING RATE TO MODEL AND KINETIC PARAMETERS

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ABSTRACT

This paper reports an investigation of the sensitivity of predicted values for the critical cooling rates for glass formation (R_c) to both model and material parameters. The values of R_c to form glassy SiO_2 and GeO_2 were calculated by avoidance of the nose of the (isothermal) TTT curve, as well as by a more rigorous method, based on crystallization statistics, which takes into account the cumulative crystallization during the cooling path. It is shown that the simplified (TTT) approach consistently overestimates R_c but provides estimates of R_c within about an order of magnitude of those given by the exact treatment. Material parameters which affect both nucleation and growth rates, such as, thermodynamic driving force for crystallization and interfacial energy can have a significant effect on R_c. The implications of the present findings for previous studies are discussed.

INTRODUCTION

Kinetic treatments of glass formation based on the general theory of transformation kinetics /1,2, e.g./ have been used extensively to predict the critical cooling rates (Rc) for forming metallic and inorganic glasses. In many cases, significant approximations are employed - both in the model used to relate the volume fraction crystallized, X, to the nucleation and crystal growth rates and in the values of these kinetic parameters for specific materials.

This article reports an investigation of the critical cooling rates to form glassy SiO_2 and GeO_2 and the dependence of predicted values of R_c on both theoretical models - by means of an exact treatment of crystallization statistics vs. the avoidance of the nose of the TTT curve - and on material parameters - interfacial free energy and the variation of thermodynamic driving force with temperature.

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INFLUENCE OF THEORETICAL MODELS ON THE CALCULATION OF X

TTT METHOD: The simplest approach to the evaluation of glass-forming ability is via the use of Time-Temperature-Transformation (TTT) diagrams. Such diagrams present the times required to produce a given volume fraction of crystals, X, as a function of temperature. The critical cooling rate for glass formation is taken as that cooling curve which is tangent to the nose of the TTT diagram corresponding to a predetermined (critical) value of crystallinity.

For small volume fractions crystallized, with time independent nucleation (I_o) and growth (U) rates, X can be calculated by the Avrami expression /1/:

$$X = (\pi/3) I_o \cdot U^3 \cdot t^4 \qquad (1)$$

where t is the elapsed time. I_o may be expressed as /3/

$$I_o = KT/\eta \exp(-K' \cdot \alpha^3/T \cdot \Delta G^2) \qquad (2)$$

where K and K' are constants, T is the absolute temperature, η is the viscosity, α is the Turnbull ratio (related to the crystal-liquid interfacial energy) and ΔG the thermodynamic driving force for crystallization.

Materials with low values of melting entropy ($\Delta S_f < 2R$) usually exhibit a normal growth mechanism; and the growth rate is given by /4/:

$$U = \frac{K''T}{\eta} [1-\exp(-|\frac{\Delta G}{RT}|)] \qquad (3)$$

where K" is a material constant and R is the gas constant. By combining eqns. (1-3) and using appropriate values for the material constants, one may obtain the TTT curve and R_o for any degree of crystallinity.

The driving force ΔG may be calculated for a constant difference between the specific heats of liquid and crystal, ΔC_p:

$$\Delta G = -T_f \Delta S_f [(1-T_r)(1-\gamma) - \gamma T_r \ln(T_r)] \qquad (4)$$

where T_f is the melting point, $T_r = T/T_f$, $\gamma = \Delta C_p/\Delta S_f$ and ΔS_f is the entropy of fusion.

CRYSTALLIZATION STATISTICS: An exact description of the volume fraction transformed, as well as numbers and size distributions of crystals, in a body subject to an arbitrary thermal history was provided by Hopper et al. /5/. This

technique, known as crystallization statistics, divides the heat treatment into a large number of smaller temperature steps. At any one temperature the transformation characteristics of the sample are determined by summing the individual isothermal transformation behavior occurring during each of the preceding steps. With this approach, the volume fraction crystallized at the time t_j is represented as

$$X(t_j) = 1-\exp\left(-\sum_{i=1}^{j} \frac{4\pi}{3} I_{oi}(t_i) r_i^3(t_j,t_i)\Delta t\right). \qquad (5a)$$

$I_{oi}(t_i)$ is the steady state nucleation frequency at time t_i and is given by eqn. (2). $r_i(t_j,t_i)$ is the value of the radii at time t_j of crystals nucleated at time t_i and is expressed as

$$r_i(t_j,t_i) = r_i^*(t_i) + \sum_{k=1}^{j} U_k(t_k)\Delta t \qquad (5b)$$

where $r_i^*(t_i)$ is the radius of the critical nuclei when it is initially formed at t_i; and U_k is the crystal growth rate at time t_k, given by eqn. (5).

COMPARISON OF TTT AND CRYSTALLIZATION STATISTICS: Table 1 compares the critical cooling rates required to form glasses of SiO_2 and GeO_2, calculated using the approximate TTT treatment and the exact method of crystallization statistics. For GeO_2, the Turnbull ratio, α, was taken as 0.39 and 0.44 (corresponding, respectively, to nucleation barriers for $\gamma = 0$ of 40 kT and 60 kT at $\Delta T_r = 0.2$); while for SiO_2, α was taken as 0.50 and 0.57 (again) corresponding to nucleation barriers of 40 kT and 60 kT at $\Delta T_r = 0.2$). It is seen that the treatment of glass formation using TTT analysis consistently overestimates R_c (as expected); but that critical cooling rates estimated using TTT analysis are typically well within an order of magnitude of R_c values obtained using the exact treatment of crystallization statistics.

Table 1. Calculated Critical Cooling Rates (K/sec) to Form Glasses of SiO_2 and GeO_2

	SiO_2		GeO_2	
	40 kT	60 kT	40 kT	60 kT
TTT	3.0 x 10-3	1.2 x 10-4	20	0.8
Crystal	4.7 x 10-4	1.6 x 10-5	3	0.1
TTT(r*)	3.8 x 10-3	1.2 x 10-4	23	0.8
Crystal(r*)	2.1 x 10-3	1.7 x 10-5	7	0.1

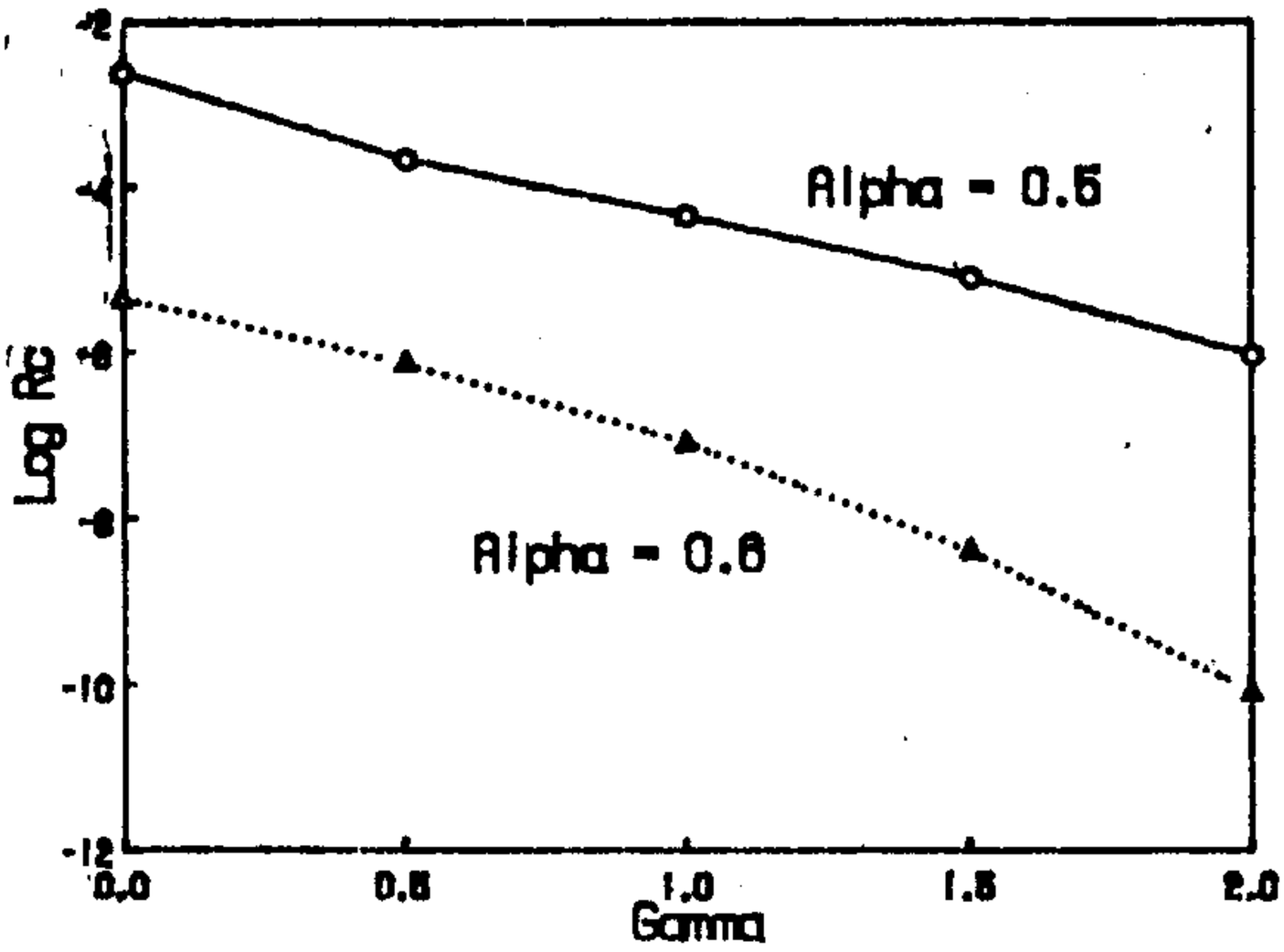

Figure 1. Log (critical cooling rate) versus gamma for SiO_2-like material and two different values of the Turnbull ratio (alpha).

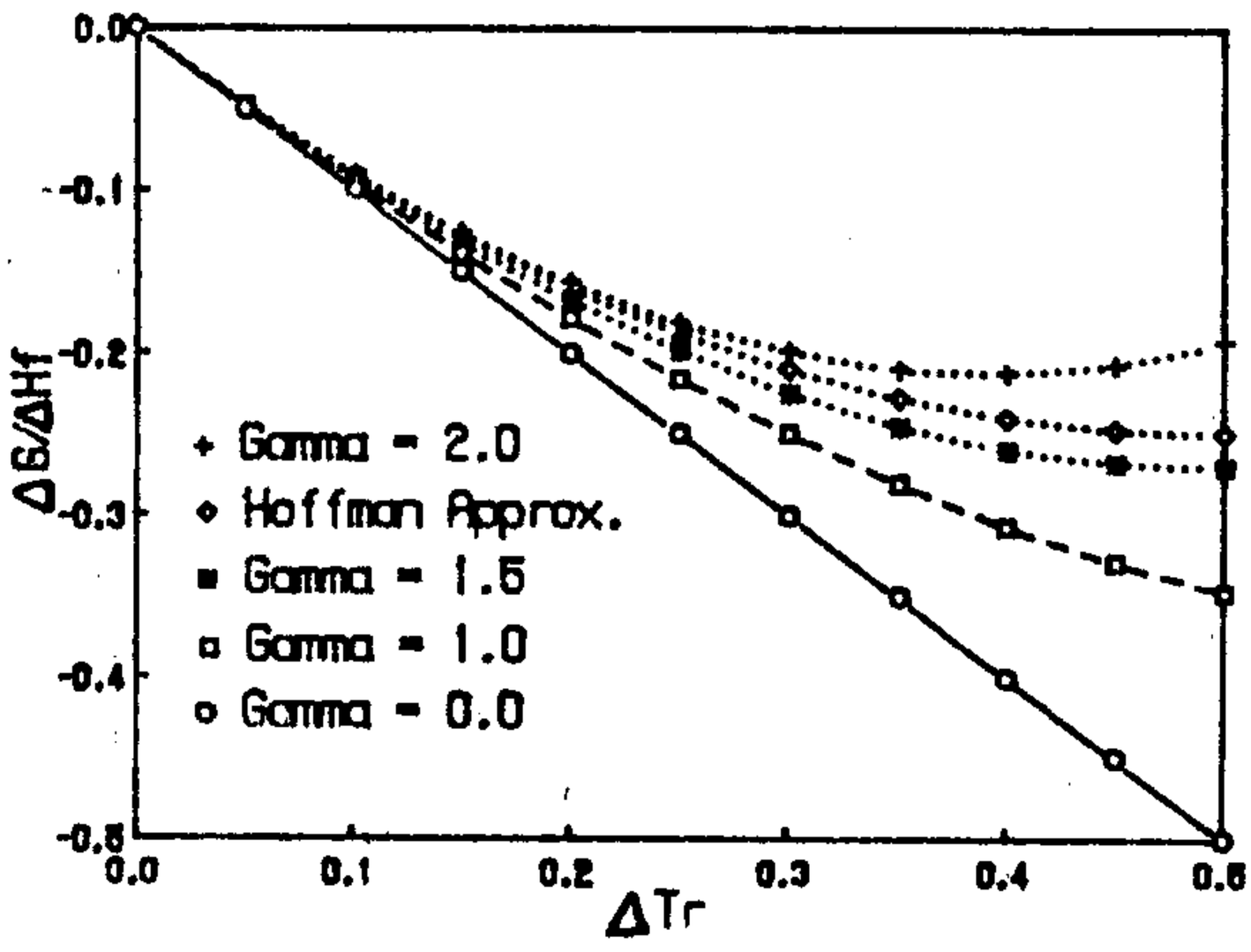

Figure 2. Reduced driving force for crystallization versus reduced undercooling for various values of gamma and for the Hoffman approximation.

Also shown in Table 1 are critical cooling rates calculated with and without consideration of the finite size of the critical nucleus. It is seen that for small (but reasonable) values of the nucleation barrier, neglect of the finite size of the critical nucleus leads to underestimates of R_c; while for larger (but reasonable) values of the nucleation barrier, the finite size of the critical nucleus has little effect on R_c.

EFFECTS OF MATERIAL PARAMETERS ON R_c

Next, the sensitivity of predicted values of R_c to changes in physical parameters which affect both the nucleation and growth rates will be explored. Fig. 1 shows the predicted values of R_c to form vitreous SiO_2 as a function of γ for $\alpha = 0.5$ and 0.6. A survey of the literature indicates that for a wide variety of materials, $0<\gamma<2$. It is seen that R_c for $\alpha = 0.5$ is larger than that for $\alpha = 0.6$ by a factor of 500-10,000, depending on the value of γ. It is also seen that increasing γ leads to lower predicted critical cooling rates, and that the dependence of R_c on γ is greater for larger values of γ.

The large undercooling approximation for ΔG originally suggested by Hoffman /6/ yields predicted critical cooling rates intermediate between those obtained using $\gamma = 1.5$ and $\gamma = 2.0$ in eqn. (4). This is reasonable in light of the $\Delta G/\Delta H_f$ vs. ΔT_r relations shown in Fig. 2. As seen there, the Hoffman approximation gives ΔG values which are intermediate between those for $\gamma = 1.5$ and $\gamma = 2.0$ at all ΔT_r.

In cases where the nucleation barrier is exceptionally large, as for the $\alpha = 0.6$, $\gamma = 2.0$ case with SiO_2 (nucleation barrier = 111 kT at $\Delta T_r = 0.2$), the nucleation rate is very small and the growth rate by comparison is quite large. Under these circumstances, a single nucleation event effectively crystallizes the sample (behavior expected for fluid melts like metals, but predicted here for SiO_2 with the assumed large nucleation barrier). In contrast, when the assumed nucleation barrier is exceptionally small (as 11 kT at $\Delta T_r = 0.2$), crystallization on cooling at R_c is dominated by the formation of copious nuclei which do not grow significantly during cooling. The nucleation barriers at which these limiting behaviors are observed (111 kT and 11 kT at $\Delta T_r = 0.2$) are unreasonably large and small, respectively; but their consideration does illustrate the range of transformation behavior associated with changes in the nucleation barrier.

DISCUSSION

The results presented in Table 1 indicate that the TTT method yields reasonable (order-of-magnitude) estimates of the critical cooling rate for glass formation. The method effectively 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 Centigrade degrees 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 gives rise to the TTT method overestimating R_c.

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 /7/. In the additivity model, the transformation rate dX/dt is a separable function of T and X /8/. It is only valid when the nucleation and growth curves substantially overlap or when site saturation occurs /7/. Despite the approximations used in the TTT and additivity models, values of the critical cooling rates calculated using these and the more precise crystallization statistics model all agree to within an order of magnitude.

The strong sensitivity of R_c to variations in α and γ can be understood if one refers to eqns. (1-4). α influences the extent of crystallization (and hence R_c) in two manners. Since $I_o \propto \exp(-\alpha^3)$, 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. 2) which in turn leads to diminished magnitudes for I_o, U and consequently R_c.

The calculations presented in the present paper were carried out to illustrate the effects 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.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to the Jet Propulsion Laboratory, the Division of Microgravity Science and Applications of NASA, and the Air Force Office of Scientific Research for the financial support of this work. E. D. Zanotto also acknowledges Capes/Fulbright for a fellowship support.

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