

A NEW INSIGHT ON THE KAUZMANN PARADOX

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ABSTRACT

A new approach is presented to check whether homogeneous crystal nucleation can occur before relaxation of supercooled liquids to a paradoxical state at the Kauzmann temperature (T_k). This possibility is tested for several reluctant and good glass forming oxides. The calculated relaxation times for structural relaxation (τ_r) and for crystal nucleation (τ_i) are of the same order at T_k and thus either phenomenon can occur first. Thus, the Kauzmann paradox survives!

INTRODUCTION

When dealing with the phenomenon of glass transition, about 45 years ago, Kauzmann [1] formulated his famous paradox: at some temperature T_k below the melting point the configurational entropy or specific volume of the undercooled liquid (after sufficiently long times of relaxation) becomes equal to that of the crystal, as shown in Figure 1.

densities above a certain critical value due to spontaneous crystallization. Around this density the relaxation time for the liquid to achieve structural equilibrium exceeded the time for significant crystallization and thus the catastrophe was avoided by spontaneous nucleation. It should be stressed, however, that hard-sphere liquids are expected to be extremely reluctant glass formers.

An interesting study was reported by Zelinski et al.[3] who calculated both structural relaxation times, τ_r , and the period for significant crystallization, τ_c , of an organic and an oxide liquid, o-terphenil and anorthite, respectively, at a temperature T_k where the extrapolated thermodynamic data indicate a paradoxical state. The relaxation times were evaluated by the following expression:

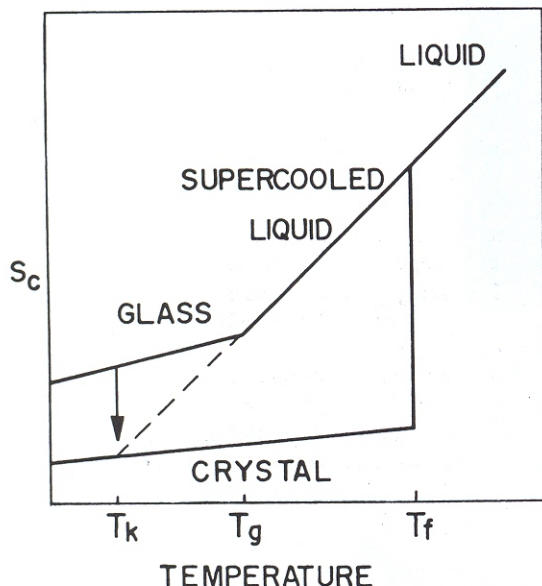


Fig.1. Configurational entropy versus temperature.

Kauzmann proposed that spontaneous crystal nucleation should occur before relaxation of the liquid to a paradoxical state. However, only a few authors have tested his proposition. For instance, in molecular dynamics simulations for a hard sphere liquid [2] it was impossible to explore the equilibrium liquid phase at

where $\tau_r(95)$ is the average time for 95% relaxation of the initial entropy difference from the equilibrium liquid, η_0 the equilibrium viscosity at a temperature T and G_0 the shear modulus ($G_0 \sim 5.10^9$ Pa for oxide glasses below T_g). This expression overestimates the structural relaxation times [3]. The crystallization times at T_k were estimated using the classical expressions for homogeneous nucleation and (normal) crystal growth. The calculations indicated that the times required for 99% crystallization are larger by a factor of 60 than those required for relaxation to a paradoxical state, and hence the paradox remains. However, taken into account the numerous approximations and extrapolations involved in the calculations, the observed difference between τ_r and τ_c (a factor of 60) is not significant.

A third important report was published by Angell et al.[4] who compared the experimental transient times for homogeneous nucleation, τ_{ex} , determined by James et al.[5] for a $Li_2O \cdot 2SiO_2$ glass, with the calculated structural relaxation times, τ_r ($10\eta_0/G_0$, a lower bound) at several temperatures above T_k . As, in the temperature range covered, both times presented Arrhenian behavior

and $\tau_{ex} \approx 10^3 \tau_r$, the authors concluded that this difference would be maintained at T_k and thus the glassy state was more rapidly assessable to the relaxing liquid than the crystalline state, and there was no escape from the impending entropy catastrophe by the route of homogeneous nucleation. The basic difficulty with this approach is that the Arrhenian behavior is not expected to hold in a wide temperature range down to T_k .

In this article a different approach is used to check the possibility that homogeneous crystal nucleation occurs before the paradoxical state at T_k . This possibility is tested for several reluctant and good glass forming oxides.

THEORY

At least one nucleation event is necessary for the occurrence of crystallization before structural relaxation. The time of birth of the first nucleus could be estimated by the ratio Nv/I , where Nv is the total number of 'molecules' per unit volume of liquid and I the steady-state nucleation rate. As transient nucleation is expected to occur in the vicinity of T_k , one may instead estimate the induction period, τ_i , before nucleation reaches the steady-state regime, having in mind that several nucleation events occur in that period. Fortunately, recent computer simulations [6] demonstrated that τ_i can be well estimated by the Kaschiev equation [7], which has been modified by James [5] to give:

$$\tau_i = (48 \alpha a^5 \Delta H_f N_A^{5/3} / \pi \Delta G^2 V_m^{2/3}) \eta \quad (2)$$

where $0.4 < \alpha < 0.6$ is the reduced surface energy (empirically determined from homogeneous nucleation measurements in oxide and metallic liquids), a the atomic jump distance, ΔH_f the heat of melting, N_A is Avogadro's number, ΔG the molar thermodynamic driving force for crystallization, V_m the molar volume and η the viscosity.

If crystal nucleation occurs below DTA-T_g, elastic stresses, associated to a strain energy γ , relax at times slightly shorter than the structural relaxation times, and cannot be neglected, thus ΔG should be replaced by $\Delta G - \gamma$ in Eq. (2). Hence, if only ΔG is used, the induction time is overestimated. In fact, Zanotto & Weinberg [8] demonstrated that equation (2) predict quite well the induction periods for nucleation in silicate glasses at the glass transition interval. However, for $T < \text{DTA-T}_g$, the region of interest in this work, the estimates of τ_i are larger than the experimental values, and the difference increases for lower temperatures. Thus, equation (2) overestimates τ_i at T_k .

Conservative overestimates for the structural relaxation times τ_r are given by equation (1). Hence, one can define a ratio $R = \tau_i / \tau_r$, which is viscosity independent, avoiding the problem of a time dependent property during structural relaxation. The ratio R is given by:

$$R = \alpha a^5 \Delta H_f N_A^{5/3} G_o / 2\pi \Delta G^2 V_m^{2/3} \quad (3)$$

If one assumes an upper bound for the driving force, $\Delta G = \Delta H_f \Delta T / T_f$, equation (3) can be rewritten as:

$$R = K (1 - T_r)^{-2} \quad (4)$$

where $K = \alpha a^5 N_A^{5/3} G_o / 2\pi V_m^{2/3} \Delta H_f$ and $T_r = T / T_f$ is the reduced temperature, which varies from 0 to 1 and hence $(1 - T_r)^{-2}$ is always ≥ 1 . Thus, if the constant K is larger than unity, then $\tau_i > \tau_r$ and relaxation of the glass to a supercooled liquid state is favored over crystal nucleation in all temperatures. However, if $K < 1$ a temperature range exists where $R < 1$ and crystal nucleation occurs faster than relaxation to a supercooled liquid.

Values of K for several reluctant and good glass forming systems were calculated and are listed in Table I. The glass formers and some intermediate oxides (Cr₂O₃, TiO₂, Ta₂O₅) have values somewhat larger than unit, and thus the paradoxical state is not avoided. On the other hand, the network modifiers and some intermediate oxides (which do not form glasses even with cooling rates up to 10^7 K/s) have K and R slightly smaller than unit at T_k . Figure 2 shows the curves of $R = \tau_i / \tau_r$ versus T_r for selected oxides, all the others falling in between them.

CONCLUSIONS

Taken into account the fact that the differences between τ_i and τ_r are small at T_k for all oxides studied, $0.2 < R < 50$, and that various approximations were necessary for the calculations, it seems that both relaxation times are of the same order and either phenomenon (structural relaxation or crystal nucleation) can occur first. Thus the Kauzmann paradox cannot be avoided by homonucleation.

On the other hand, it is quite interesting the fact that all glass formers have $K > 1$ while the modifier oxides (extremely reluctant glass formers) have $K < 1$, indicating that crystal nucleation is favored in these systems, in agreement with experimental practice (glasses cannot be formed due to fast crystallization). Thus, it may be interesting to check in more detail if K is a good parameter to define glass forming ability.

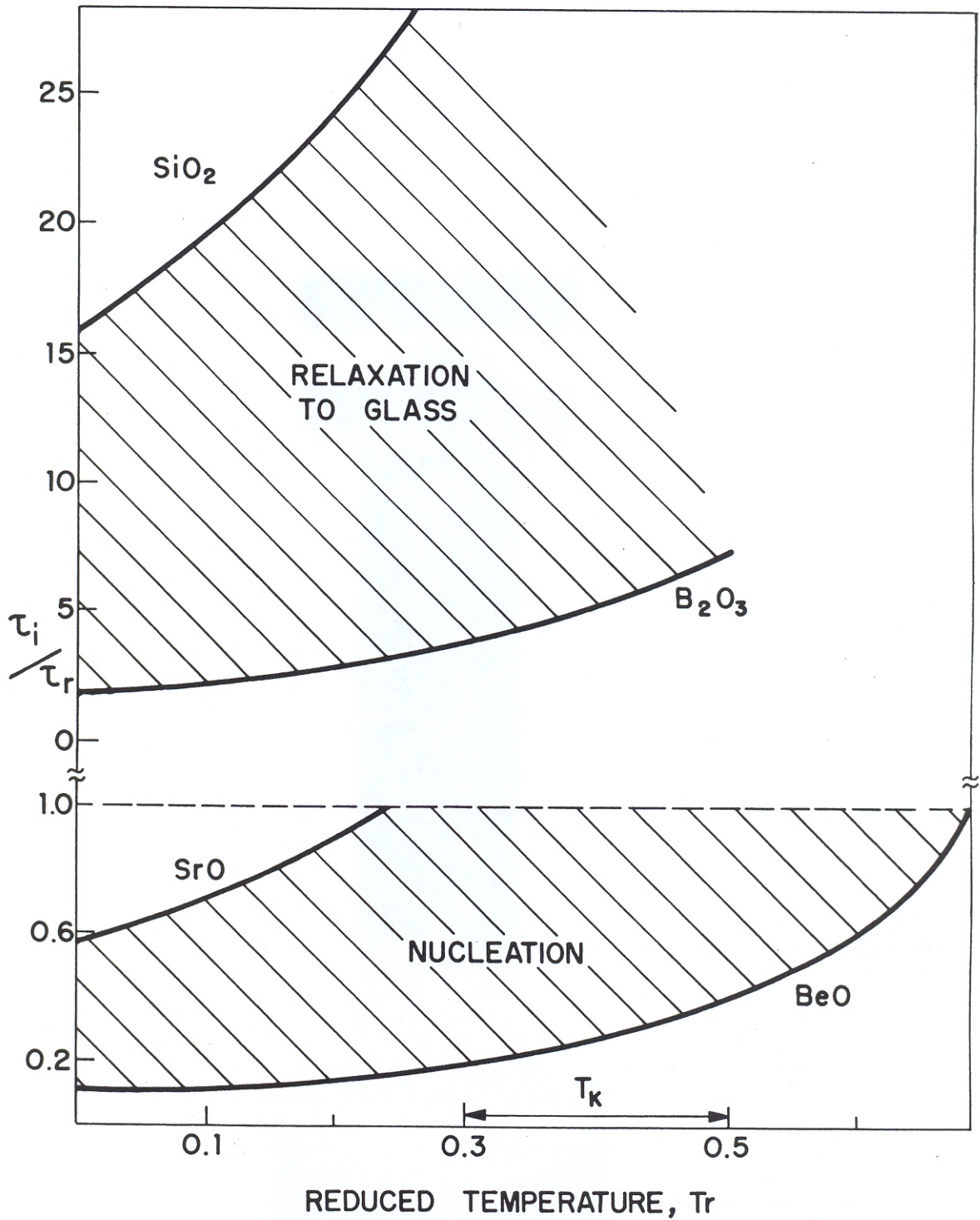


Fig. 2. Ratio of induction time for nucleation and relaxation time, $R = \tau_i/\tau_r$, as a function of reduced temperatures for good glass formers (SiO_2 and B_2O_3) and modifier oxides (SrO and BeO).

Table I - Properties of various reluctant and good glass formers

System	$\lambda(\text{\AA})$	ΔH_f J/mol	$V_m \times 10^5$ m^3/mol	K
Good Glass Formers				
SiO ₂	7.1	15000	2.5	15.9
Na ₂ O. Al ₂ O ₃ . 6SiO ₂	8.7	55000	2.1	13.4
GeO ₂	4.9	15100	3.0	2.2
B ₂ O ₃	5.1	22600	2.8	1.9
Intermediates				
Cr ₂ O ₃	6.6	17600	2.9	8.5
TiO ₂	6.4	47800	1.9	3.4
Ta ₂ O ₅	8.0	201100	5.5	1.3
Al ₂ O ₃	5.7	109000	2.6	0.7
V ₂ O ₅	5.6	65400	5.4	0.7
ZrO ₂	5.2	87000	2.0	0.5
Modifiers				
BeO	3.0	71200	0.8	0.1
MgO	4.2	77500	1.1	0.4
CaO		51100	1.7	
SrO	4.9	70000	2.2	0.6
BaO		57800	2.7	

* $\lambda \approx V_{uc}^{1/3}$, V_{uc} = unit cell volume
 $K = 1.127 \times 10^{48} \lambda^5 / (V_m^{2/3} \Delta H_f)$, SI units

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