Do cathedral windows flow? Additional Remarks

In the first part of this article, Brazilian scientist Edgar Dutra Zanotto, concluded that the flow of glass could not be the cause of the observed variation in thickness in cathedral windows. However, the response to his first article has led him to revise his original estimate of the relaxation time at room temperature for a window glass.

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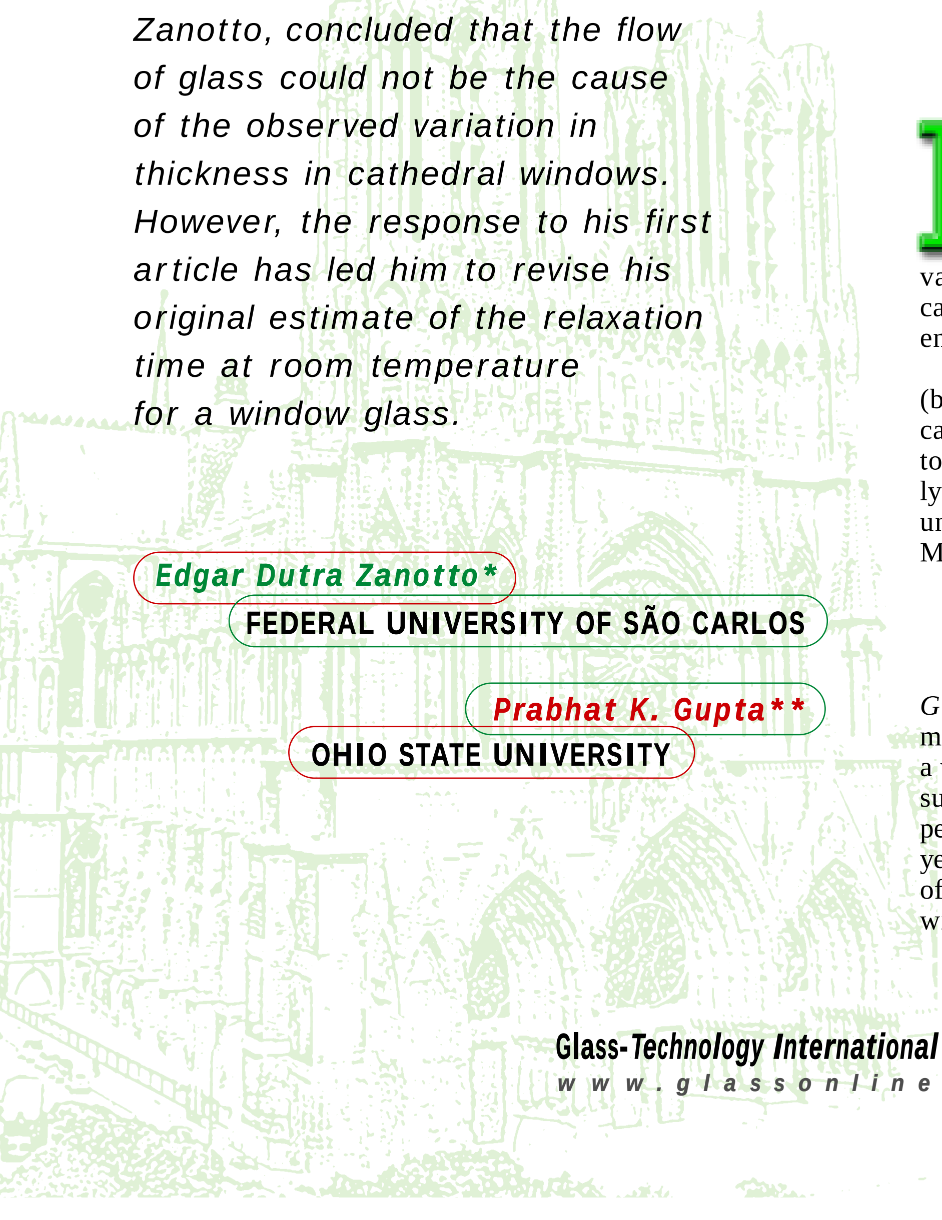


INTRODUCTION

Zanotto's[1] conclusion that the flow of glass could not be the cause of the observed variation in thickness in cathedral windows caused widespread response from both the scientific community and science magazines[2-5].

In the first part he contradicted the widely held (but not by all)[6] belief that because medieval cathedral glass windows are thicker at the bottom than at the top, window glass flows slowly (over hundreds of years) at room temperature under the influence of gravity. He used the Maxwell relaxation time

$$\tau(T) = \eta(T)/G(T) \qquad (1)$$

where η is the viscosity at temperature T and G the infinite frequency shear modulus, to estimate the time for glass to flow noticeably, and a value of the 'equilibrium' viscosity (of the supercooled melt) extrapolated to room temperature, T_r, to conclude that $\tau(T_r)$ is at least 10^{32} years, and so the flow of glass cannot be the cause of the observed thickness variation in cathedral windows.

Do cathedral windows flow? Additional Remarks

The most serious of the responses to these conclusions was a comment by P. Gupta, the second author of the present article, that the use of 'equilibrium' viscosity only gives an upper bound for $\tau(T_r)$. Therefore the question of whether window glass flows at room temperature remains unresolved.

Gupta also pointed out that the use of isostructural viscosity (i.e., the viscosity of the glassy state where the structure is frozen) - instead of the equilibrium viscosity - extrapolated to T_r should give a more realistic estimate of $\tau(T_r)$. Here it is reported that such a revised estimate of $\tau(T_r)$ using the isostructural viscosity data for the window glass composition shows that, even though the revised $\tau(T_r)$ is several orders of magnitude less than the value estimated by Zanotto, his conclusion that cathedral window glass does not flow at room temperature still remains valid.

TABLE 1

CHEMICAL COMPOSITION OF DIFFERENT GLASSES

	H&S	MAZURIN	MEDIEVAL
SiO_2 (wt.%)	71.6	72.7	45.0-75.0
Al_2O_3	1.6	1.3	0.8-2.0
CaO	7.9	8.6	1.0-25.0
MgO	3.8	3.4	0.8-8.0
Na_2O	13.7	13.6	0.1-18.0
K_2O	0.5	0.4	2.0-25.0
TiO_2	0.3	na	na
Fe_2O_3	0.1	na	0.3-2.1
SO_3	0.3	na	na

na = not available
H&S = window glasses used by Hara & Suetoshi[13]
Mazurin = window glasses used by Mazurin et. al[7]

DISCUSSION

Isostructural viscosity

Following a jump in temperature at constant pressure, the properties of a viscous liquid continue to change with time even after thermal equilibrium has been reached. This slow change is known as structural relaxation and reflects the time required for the structure to rearrange into its new "equilibrium" configuration.

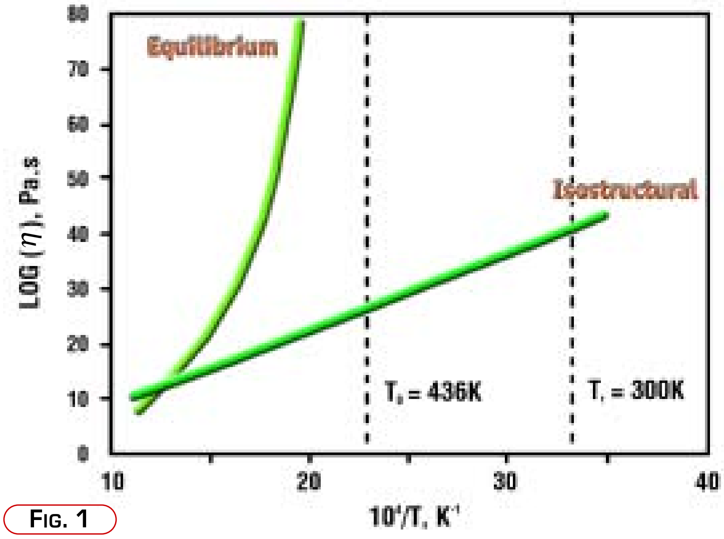


FIG. 1

Temperature variations of the equilibrium and isostructural viscosities of the window glass based on Eq. (4).

The average structural relaxation time, τ_s, increases very rapidly with the decrease in the temperature of the supercooled liquid state. As a consequence, when a liquid is cooled at some constant rate, q, its structure remains in equilibrium within the time scale of observation characterized by

$$\sim 1/q) \quad \text{for } T > T_f(q)$$

the fictive temperature (see Appendix A). The structure falls out of equilibrium and is frozen for $T < T_f(q)$ where τ_s becomes larger than the observation time. For typical cooling rates used in glass forming, $T_f(q)$ is given approximately by the glass transition temperature, T_g (temperature for which the equilibrium viscosity is 10^{12} Pa.s). The properties of a supercooled liquid assume their 'equilibrium' values above $T_f(q)$ and 'isostructural' values below $T_f(q)$ and show transition between the two in the vicinity of $T_f(q)$. For example, the first order thermodynamic properties, such as density, show a change in slope while the second order properties, such as heat capacity, show discontinuities. The equilibrium and isostructural behaviours of the viscosity are shown in Figure 1 for a window glass composition (see also Table 1). The parameters are those reported by Scherer (Ref.

12) and T_f = 816 K. The isostructural data were measured by Mazurin et al[7] near the glass transition temperature T_g. Figure 1 shows that the equilibrium viscosity of window glass diverges at a temperature above T_r while the isostructural viscosity remains finite at room temperature.

Extrapolation of isostructural viscosity to room temperature

In order to calculate $\tau(T_r)$, it is necessary to extrapolate the isostructural viscosity from the temperatures in the region of T_g (about 820 K) where experimental measurements were made, down to the room temperature. Mazurin's measurements indicated that the isostructural viscosity follows an Arrhenius temperature dependence. This was confirmed by Scherer[8] who also examined the structural relaxation data in glasses. Scherer also concluded that the Adam-Gibbs theory[9] (Appendix B) provides the most reasonable description for the temperature dependence of both the equilibrium and the isostructural viscosities.

According to the Adam-Gibbs model the viscosity is

$$\eta = \eta_0 \exp[A/TS_c] \qquad (2)$$

where A and η_0 are constants. The configurational entropy, S_c, is given by:

$$S_c(T_f) = \int_{T_0}^{T_f} (\Delta c_p/T)\, dT \qquad (3)$$

Here Δc_p is the difference in heat capacity between the equilibrium liquid and the frozen glass, T_0 is the Kauzmann temperature defined such that $S_c(T_0) = 0$. Equation (3) shows that the configurational entropy of the frozen state is governed by the fictive temperature, T_f.

As shown recently by Richert and Angell[10], Δc_p, in the vicinity of T_g, is well approximated by B/T, where B is a constant. Equations (2) and (3), then, lead to

$$\eta = \eta_0 \exp[Q/(T(1-T_0/T_f)] \qquad (4)$$

where $Q = AT_0/B$. For equilibrium supercooled liquid, $T_f = T$ and Equation (4) reduces to the Vogel-Fulcher-Tamman equation (described in Ref. 1). For the isostructural state, T_f is constant and Equation (4) reduces to the Arrhenius equation. The validity of the Adam-Gibbs model has been well established[11].

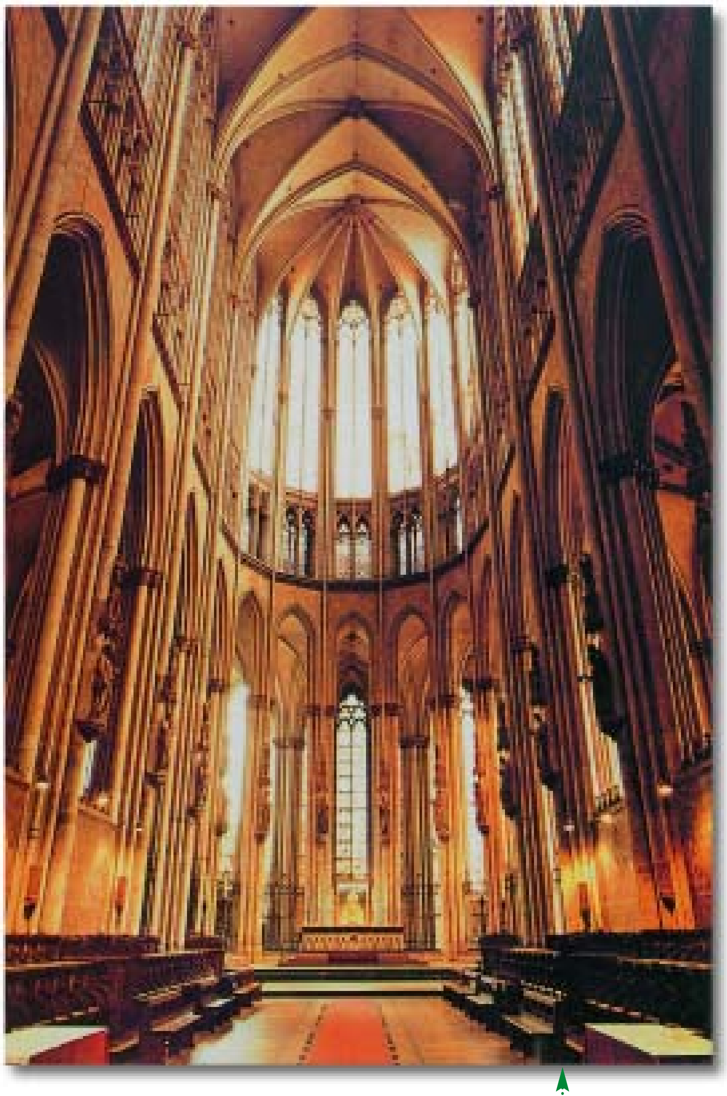
To use Equation (4), one needs to establish the values of the parameters Q, T_0, and η_0 for the window glass. Fortunately, Scherer[12] has determined the values of these parameters by carefully analysing the volume (density) relaxation data of Hara and Suetoshi[13] in a soda-lime-silica plate glass (composition given in Table 1) as well as Mazurin's isostructural viscosity data in terms of Equation (4). The values of the parameters as reported by Scherer for the glass used in Ref. 13 are:

$$\eta_0 = 9\text{x}10^{-6}\ \text{Pa.s},\ Q = 14{,}900\ \text{K, and}\ T_0 = 436\ \text{K.}$$

As is clear from Figure 1, the value of the isostructural viscosity at room temperature depends on the fictive temperature. The higher the T_f, the lower the value of isostructural η at T_r. Therefore, we need to establish the fictive temperature of the cathedral glass. Since the cathedral windows were annealed after forming, the fictive temperature of the cathedral windows must be less than the temperature where the equilibrium viscosity is $10^{12.4}$ Pa.s[14]. To be on the conservative side, we assume T_f equal to T_g, where the equilibrium viscosity is 10^{12} Pa.s. For the Hara and Suetoshi composition, this corresponds to a temperature of 816 K.

Taking T_r = 300 K, T_f = 816 K, and $G(T_r)$ = 30 GPa[15] in Equations (1) and (4), one obtains: $\tau(T_f) \sim 2 \text{ x } 10^{23}$ years. This value, although 8 orders of magnitude less than the original estimate of Zanotto, still implies that the dimensional variations of the cathedral glass windows are not caused by cold flow of glass.

There remains the question as to what is the cause of the suggested (but never reported in a scientific periodical) dimensional non-uniformities in cathedral glass windows. We now know that it is not because of the flow of glass. It was speculated[1] that ancient window glasses were blown into cylinders that were split and flattened manually. Hence, the pieces were not uniform in thickness and some lower parts could be thicker than the upper parts.



Cologne Cathedral, Germany, 13th century

Another possibility mentioned by Hares[16] is that window glasses made by the crown process had "a thickness that decreased with increasing distance from the centre". It is quite possible that some cathedral window makers installed the cut up window panes with thicker side at the bottom[17].

CONCLUSION

The revised estimate shows that window glass will only flow appreciably at room temperature if one waits until the "Second Coming"!

ACKNOWLEDGMENTS

EDZ acknowledges encouragement and critical comments of professors Francisco A.B. Coutinho, Luis N. Oliveira and José F. Perez of FAPESP (Brazil). He also acknowledges funding by CNPq and PRONEX.

PKG acknowledges meaningful discussions with Prof. Arun K. Varshneya of Alfred University, NY.

APPENDIX A

Fictive temperature (T_f) of a glass

Tool[18] introduced the concept of fictive temperature to characterize the non-equilibrium structure of a glass. It is defined as the temperature where the structure of the corresponding equilibrium liquid (normal or supercooled) is the same as that of the given glass. Sometimes, T_f is referred to as the structural or the configurational temperature. Glasses of same composition showing different values of a property have different fictive temperatures. Fictive temperature of a glass is determined by its history of formation from the liquid state.

The notion that the structure of a glass can be characterized by a single parameter such as T_f is an approximate one. Only for an idealized history, when a liquid is cooled very slowly down to a temperature T_f and is then rapidly quenched to the room temperature, can the structure of the glass be described by T_f.

In general, one parameter is not sufficient to describe the structure of a glass. This is evidenced by the fact that for the same glass different properties show different fictive temperatures. For this reason, Narayanaswamy[19] redefined fictive temperature of a property p, as follows

$$p_g(T) = p_e(T_f) + \int_{T_f(p)}^{T} (\partial p/\partial T)_g \, dT.$$

Here the subscript g refers to the isostructural (i.e., glassy) state, and the subscript e refers to the (equilibrium) supercooled liquid. For typical laboratory cooling rates, the values of $T_f(p)$ for different properties are somewhat different, but all are close to the glass transition temperature, T_g where the viscosity is 10^{12} Pa.s.

APPENDIX B

The Adam-Gibbs model

The Adam-Gibbs model is based on the idea that relaxation requires cooperative rearrangement of a group of n molecules. As the temperature drops and the liquid becomes denser, movement of one molecule disturbs an increasingly larger number of its neighbours. Adam and Gibbs[9] assumed that the barrier to rearrangement increased in proportion to n, and determined the temperature dependence of n in terms of the configurational entropy, S_c. Their result for the viscosity is

$$\eta = \eta_0 \exp[\Delta\mu 1n(w^*)/TS_c] \qquad (1)$$

where η_0 is a constant, $\Delta\mu$ is the potential barrier per molecule hindering rearrangement, w^* is the number of configurations available to the smallest group of atoms that can undergo a cooperative rearrangement ($w^* \sim 2$).

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