

Do cathedral glasses flow?—Additional remarks

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We present a revised estimate of the relaxation time at room temperature for a window glass based on extrapolated isostructural viscosity data. This estimate, while several orders of magnitude less than the previous estimate of Zanotto [Am. J. Phys. **66** (5), 392–395 (1998)], supports his conclusion that window glass cannot flow at room temperature in human time scales. © 1999 American Association of Physics Teachers.

I. INTRODUCTION

One of us, Zanotto,¹ recently examined the validity of the widely held (but not by all²) 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. Using the Maxwell relaxation time:

$$\tau(T) = \eta(T)/G(T), \quad (1)$$

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 . Zanotto argued that $\tau(T_r)$ is at least 10^{32} years. He concluded that flow of glass could not be the cause of the observed thickness variation in cathedral windows.

There was an immediate response to the article from both the scientific community and science magazines, see for instance Refs. 3–6. Scientists throughout the world made numerous questions and remarks. However, the most relevant of these 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 whether the window glass flows at room temperature remains unresolved.

Gupta also pointed out that the use of the 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 $\tau(T_r)$. In this communication, we report such a revised estimate of $\tau(T_r)$ using isostructural viscosity data for the window glass composition. We show 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.

II. DISCUSSION

A. 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. The average structural relaxation time,

τ_s , increases very rapidly with decrease in the temperature in 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 $\sim 1/q$) 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 approximately given 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 behaviors of the viscosity are shown in Fig. 1 for a window glass composition (see Table I). 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_g while the isostructural viscosity remains finite at room temperature.

B. Extrapolation of the isostructural viscosity to the room temperature

In order to calculate $\tau(T_r)$, it is necessary to extrapolate the isostructural viscosity from the temperatures in the neighborhood of T_g (about 820 K) where experimental measurements were made, down to 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 theory⁹ (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

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

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

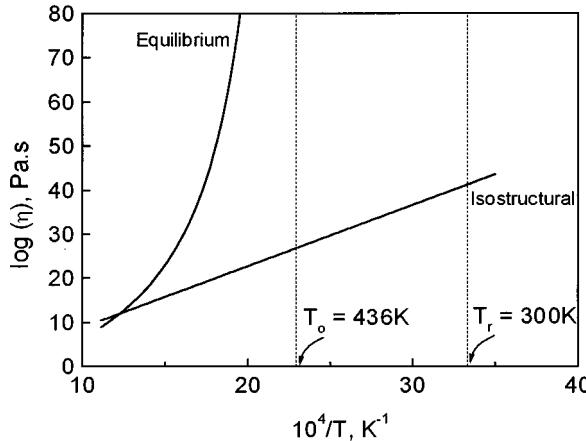


Fig. 1. Temperature variations of the equilibrium and isostructural viscosities of the window glass based on Eq. (4). The parameters are those reported by Scherer (Ref. 12) and $T_f = 816$ K.

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

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 fictive temperature, T_f , governs the configurational entropy of the frozen state.

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

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

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

To use Eq. (4), one needs to establish the values of the parameters Q , T_0 , and η_0 for the window glass. Fortunately, Scherer¹² has determined the values of these parameters by carefully analyzing the volume (density) relaxation data of Hara and Suetoshi¹³ in a soda-lime-silica plate glass (composition given in Table I) as well as Mazurin's isostructural viscosity data in terms of Eq. (4). The values of the parameters as reported by Scherer for the glass used in Ref. 13 are: $\eta_0 = 9 \times 10^{-6}$ Pa s, $Q = 14900$ K and $T_0 = 436$ K.

As is clear from Fig. 1, the value of the isostructural viscosity at room temperature depends on the fictive temperature. The higher the T_f , the lower is 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 annealing temperature (generally taken as the temperature for which the equilibrium viscosity is $10^{12.4}$ Pa s¹⁴). 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 $G(T_r) = 30$ GPa¹⁵ in Eqs. (1) and (4), one obtains: $\tau(T_f) \sim 2 \times 10^{23}$ years. This

Table I. Chemical composition (wt %) of medieval glasses and of window glasses used by Hara and Suetoshi, HS (Ref. 13) and by Mazurin *et al.* (Ref. 7). (na=not available.)

| | HS | Mazurin | Medieval |
|--------------------------------|------|---------|-----------|
| SiO ₂ | 71.6 | 72.7 | 45.0–75.0 |
| Al ₂ O 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 ₂ O | 13.7 | 13.6 | 0.1–18.0 |
| K ₂ O | 0.5 | 0.4 | 2.0–25.0 |
| TiO ₂ | 0.3 | na | na |
| Fe ₂ O ₃ | 0.1 | na | 0.3–2.1 |
| SO ₃ | 0.3 | na | na |

value, although several 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) dimensional nonuniformities in cathedral glass windows. We now know that it is not because of the flow of glass. We speculated in Ref. 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. 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 center.” It is quite possible that the cathedral window makers installed the cut up windowpanes instinctively with thicker side at the bottom.¹⁷

III. CONCLUSION

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

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APPENDIX A: FICTIVE TEMPERATURE (T_f) OF A GLASS

Tool¹⁸ introduced the concept of fictive temperature to characterize the nonequilibrium 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 the same composition showing different values of a property have different fictive temperatures. The 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, Narayanaswamy¹⁹ redefined fictive temperature of a property p , as follows:

$$p_g(T) = p_e(T_f) + \int_{T_f(p)}^T (\partial p / \partial T)_g dT. \quad (\text{A1})$$

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 occurs by the internal cooperative rearrangement of independent regions of n molecules. As the temperature drops, movement of one molecule disturbs an increasingly larger number of its neighbors. Adam and Gibbs⁹ assumed that the barrier to rearrangement is proportional to n , and determined the temperature dependence of n in terms of the configurational entropy, S_c . Their result for the viscosity is

$$\eta = \eta_0 \exp[\Delta\mu \ln(w^*)/TS_c], \quad (\text{B1})$$

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 ($w^* \sim 2$).

^aHome-page: <http://www.nit.ufscar.br/lamav>

¹Edgar D. Zanotto, “Do cathedral glasses flow?,” Am. J. Phys. **66**, 392–395 (1998). *Erratum:* The stretched exponential equation on page 392 of this paper should read: $p(t) = p_0 \exp[-(t/t_0)^\beta]$.

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¹³Morihisa Hara and S. Suetoshi, “Density change of glass in the transformation Range,” Rep. Res. Lab., Asahi Glass Co. Ltd. **5**, 126–135 (1955).

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¹⁵Narottan P. Bansal and Robert H. Doremus, *Handbook of Glass Properties* (Academic, New York, 1986), p. 322.

¹⁶George B. Hares, “3500 years of glassmaking” in *Commercial Glasses*, edited by D. C. Boyd and J. F. MacDowell (ACerS, 1986).

¹⁷Arun K. Varshneya (personal communication).

¹⁸Arthur Q. Tool, “Variations caused in the heating curves of glass by heat treatment,” J. Am. Ceram. Soc. **14**, 276 (1931).

¹⁹See, for example, George W. Scherer, *Relaxation in Glasses and Composites* (Wiley, New York, 1986), p. 116.

WHAT DO WE WANT FROM PHYSICS?

Physicists have always claimed that their science is ethically neutral. But in recent years, philosophers of science—particularly feminist philosophers—have challenged this claim. Knowledge, they say, is not neutral, but always the fruit of some intention, whether consciously recognized or not. ...Rather than leaving physicists to tell us what they want to do and just handing over the money to do it, as a society we must be involved in deciding what we want from physics and what purposes we want it to serve. We must *consciously* move it back to a more socially responsible grounding.

Margaret Wertheim, *Pythagoras' Trousers—God, Physics, and the Gender Wars* (Random House, New York, 1995), pp. 251–252.