Do cathedral glasses flow?

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(Received 23 April 1997; accepted 27 October 1997)

A general belief among members of the scientific community is that glass articles can be bent irreversibly and that they flow at ambient temperature. This myth is mostly based on widespread stories that stained-glass windows of medieval cathedrals are thicker in the lower parts. In this paper I estimate the time periods required for glass to flow and deform at ordinary temperatures, using calculated viscosity curves for several modern and ancient glass compositions. The conclusion is that window glasses may flow at ambient temperature only over incredibly long times, which exceed the limits of human history. © *1998 American Association of Physics Teachers.*

I. INTRODUCTION

Is glass a liquid or is it not? While teaching materials science and technology courses over the last two decades, I have been asked that question by students and colleagues on several occasions, because they had heard that 800-year-old stained-glass windows of 12th century cathedrals were thicker in their lower part, which suggests a downward flow of glass at room temperature. It is interesting to note that no one knew the source of this information.

At first I thought, that the above-described interpretation was a Brazilian myth, however, I later discovered that a colleague had also heard that story in Argentina.[1] A referee of the American Journal of Physics confirmed that the same story is widespread in the USA. The narrative is also emphasized in at least one American journal.[2] Additionally, a textbook of materials science,[3] and even the prestigious Encyclopedia Britannica,[4] allude to this phenomenon, stating that glass pieces bent over a period of several months at ordinary temperatures will not return to their original shape. Although some scientists may know the truth or could infer it by using simple arguments, to my knowledge there are no published calculations on the subject. Thus it appears that the alleged flow of ancient window glasses, or more generally, of the permanent deformation of glass at room temperature, is a quite universal concept and therefore merits clarification.

In this communication I use simple concepts of physics to demonstrate that typical window glasses, which contain $K_2O–Na_2O–CaO–MgO–Al_2O_3–SiO_2$ and a certain amount of impurities, may flow appreciably at ordinary temperatures only in inaccessible times, over geological periods, not within the limits of human history.

II. THEORY

Viscous fluids easily show detectable relaxation phenomena—the change of any measurable property with time following a perturbation. To a good approximation, a number of relaxation processes may be described by a modified Maxwell expression, a stretched exponential equation having the form $p(t)=p_0e^{(-\beta t/\tau)}$ (e.g., $0.5<\beta<1$ for stress relaxation in glasses), where p_0 is the initial value of a given property, $p(t)$ is the relaxed value after an elapsed time, t, and τ is the characteristic relaxation time. Thus, when $t=\tau$, $p(t)$ has relaxed to approximately 60%–37% of its original value, depending on the magnitude of β.

The viscosity coefficient or simply viscosity, η, of a liquid is one measure of the relaxation time τ. It gives an approximation to the rate of structural change and the dependence of this rate on temperature. The viscosity is related to an average relaxation time, $\langle\tau\rangle$, for bulk thermodynamic properties by

$$\langle\tau\rangle=C\eta, \tag{1}$$

where C is some constant that depends on the property being studied—enthalpy, volume, stress, etc. For a shear relaxation time, C is the inverse of the infinite frequency shear modulus, G_∞. Equation (1) indicates that all bulk structural relaxation processes of the liquid have, on the average, the same temperature dependence, and experimentally this seems to be the case.[5] An approximate derivation of Eq. (1) is given in the Appendix. For typical compositions of window glasses, G_∞ is about 30 GPa from the absolute zero to the glass transition range.[6]

The viscosity, however, varies significantly with composition and temperature. As for several other thermally activated processes, the viscosity could, in principle, be described by an Arrhenius-type expression:

$$\eta(T)=\eta_0\exp(E_\eta/kT), \tag{2}$$

where E_η is the activation energy for viscous flow, η_0 is a constant, k is the Boltzmann constant, and T is the absolute temperature. However, as the structures of most glasses vary with temperature, the activation energies also vary, and thus one cannot use an Arrhenian expression to calculate the viscosity. Exceptions have only been reported for very few (pure) network glass forming oxides, such as SiO_2, GeO_2, and P_2O_5 glass, for which the structure is temperature independent. Hence, the viscosity versus temperature curves of most glasses are usually described by an empirical expression of the Vogel–Fulcher–Tamman (VFT) type:

$$\log\eta=A+B/(T-T_0), \tag{3}$$

where A, B, and T_0 are empirical parameters which depend solely on the glass composition.

Physical insight into Eq. (3) is given by the free-volume theory summarized in Appendix 2, which assumes that the ‘‘flow units’’ (groups of molecules that flow simultaneously) cannot jump if the volume of neighboring vacancies is smaller than their own volume. Such a situation is observed at a characteristic temperature T_0 where the viscosity tends to infinity.

Table I. Typical compositions (wt %) and VFT parameters[a] of window glasses.

	Modern	Medieval glasses
SiO_2	73.2	45–75
Na_2O	13.4	0.1–18
CaO	10.6	1.0–25
Al_2O_3	1.3	0.8–2.0
K_2O	0.8	2.0–25
MgO	0.7	0.8–8.0
Fe_2O_3	0.1	0.3–2.1
MnO	⋯	0.3–2.3
P_2O_5	⋯	2.5–10
A	−2.6	−4.2[a]
B	4077.7	5460.9[a]
T_0	254.7	196.3[a]

[a] Yellow glass of the Gatien Cathedral, Tours (France).

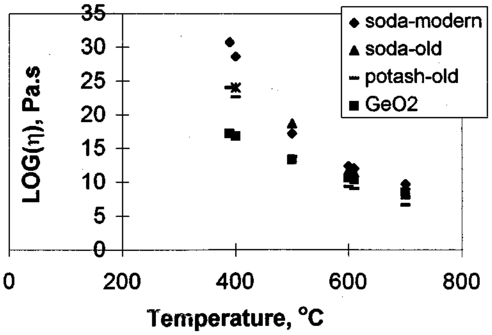

Fig. 1. Viscosity of different glasses as a function of temperature.

III. CALCULATIONS AND RESULTS

Table I shows typical compositions of both modern and medieval window glasses. While the compositions of the former are relatively uniform, the compositions of ancient glasses vary enormously, as reported in Ref. 7, where about 350 glasses were analyzed. In general, medieval window glasses have a higher level of impurities, such as iron and manganese, and are potassium rich, while contemporary window glasses are richer in sodium.

An important characteristic of glasses is that they do not have any microstructural features, such as crystal phases, grain boundaries, pores, etc., which depend on both processing conditions and chemical composition. Hence, several bulk properties of glasses, e.g., thermal expansion coefficient, density, refractive index, and viscosity are additive functions which solely depend on the chemical composition. Therefore, numerical coefficients which relate a given property to the glass composition can be empirically determined. Indeed, handbooks[6] and commercial software are available, which are extensively used by the glass industry to estimate several properties from a knowledge of the glass chemical analysis. One of the most successful and widely used procedures is due to Lakatos *et al.*,[8] which relates the content of K_2O, Na_2O, CaO, MgO, Al_2O_3, and SiO_2 in a glass to its Vogel–Fulcher–Tammann parameters A, B, and T_0.

The VFT constants of Table I were calculated using the Lakatos formulas,[8] neglecting the effect of minor impurities. This procedure will probably lead to slightly overestimated values of viscosity. However, it will not have any significant effect on the ''order of magnitude'' calculations presented here. For instance, for a yellow potash glass of the Gatien Cathedral, Tours (France), the estimated VFT constants are: $A=-4.22$, $B=5460.9$, and $T_0=196.3$ °C. The viscosity (in Pa s) can be obtained by Eq. (3). The calculated viscosity curves of a typical contemporary glass, two medieval glasses, and a GeO_2 glass are plotted in Fig. 1.

Despite being capable of describing quite well the temperature dependence of flow resistance over several decades in viscosity, from the melting range (1400–1500 °C) to the glass transition range ($T_g \sim 550-600$ °C), a complicating factor arises with Eq. (3) because $T_0(180-360$ °C) is well above room temperature, T_a. Hence, Eq. (3) predicts an infinitely large viscosity at that temperature. Evidently, a different flow mechanism could occur below T_0 (for instance, small molecules or even individual atoms instead of molecules or ''flow units'' may diffuse independently) and thus another, unavailable, equation should be used to estimate the relaxation times at room temperature. In spite of this fact, one can estimate what the necessary temperature would have to be to observe significant viscous flow in a time span of a few centuries. By using Eqs. (1) and (3) and the data for the French glass, one concludes that it is necessary to heat a typical medieval glass to approximately 414 °C to observe a significant flow in 800 years.

A numerical calculation of the relaxation time at T_a, albeit approximate, can be made by referring to the viscosity of GeO_2 glass, which has an equivalent transition temperature to window glass (Fig. 1). For GeO_2 glass, the viscosity can be described by an Arrhenius-type equation, and hence, one can extrapolate the viscosity curve down to room temperature to estimate $\eta(T_a)$. By substituting $\eta(T_a)$ in Eq. (1), one has a *lower bound* for the relaxation time of window glass because, on decreasing temperature, the viscosity of GeO_2 does not rise as quickly as that of window glass (Fig. 1).

The viscosity of GeO_2 glass may be adequately described by Eq. (3) with $A=-9.94$ and $B=17\,962$ (η [Pa s]; T[K]) and $T_0=0$.[9] Therefore, the predicted relaxation time for GeO_2 at room temperature is 10^{32} yr. Hence, the relaxation period (characteristic flow time) of cathedral glasses would be even longer. In fact, that period is well beyond the age of the Universe ($\sim 10^{10}$ yr)!

One might argue that the impurities of medieval glasses (which are not taken into account by the Lakatos formulas) could lower the viscosity to levels which would lead to a much faster flow than anticipated. However, even assuming a plausible decrease in the viscosity of one or two orders of magnitude, that would not alter the conclusions of the previous calculations. Additionally, the effect of weathering and leaching of the medieval glass windows during several centuries might seem important; however, that process only leads to a superficial chemical attack and only diminishes the glass shine and transparency but has no significant effect on viscosity and other bulk properties.

Experimental evidence to reinforce the idea of large relaxation times at room temperature is the fact that glass vases from thousands of years ago remain undeformed in museums around the world. The possibility that some cathedral glasses are thicker at their bottom may be explained by the fact that ancient window glasses were blown into cylinders that were

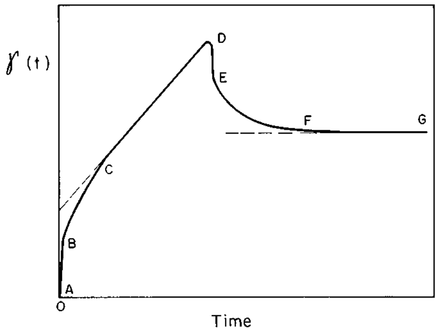

Fig. 2. Schematic behavior of the deformation $\gamma(t)$ of a viscoelastic material under constant stress.

split and flattened manually. Hence, the pieces were not uniform in thickness and some lower parts could be thicker than the upper parts.

IV. CONCLUSION

As a result of the previous discussions, it can be concluded that medieval and contemporary window glasses cannot flow at room temperature in human time scales!

ACKNOWLEDGMENTS

I am indebted to Professor F. A. B. Coutinho, Professor L. N. Oliveira, and Professor J. S. Sintra for stimulating discussions on the subject. Thanks are also due to CNPq and to PRONEX for financial support.

APPENDIX

1. Empirical theory of viscoelasticity

Assuming the Burgess model of viscoelasticity,[5] let us consider a creep experiment in which a constant shear stress τ_0 is suddenly applied to a viscous liquid. The experimentally observed behavior of the deformation $\gamma(t)$ under constant stress consists of three parts, schematically shown in Fig. 2:

$$\gamma(t)/\tau_0=[1/G_\infty+h(t)+t/\eta], \tag{A1}$$

where $1/G_\infty$ refers to the instantaneous elastic response (segment AB in Fig. 2), $h(t)$ is the recoverable delayed elasticity $[h(0)=0,\ h(\infty)=\text{constant, segment } BC]$, and the third term refers to the irrecoverable viscous deformation (segment CD). If the stress is suddenly released, instantaneous recovery occurs (segment DE) followed by a relaxation period represented by segment EF and governed by the relaxation function $\phi(t)$. The relaxation function is an intrinsic property of the material under study. The right-hand side of Eq. (A1) is defined as the compliance of the Burgess model, $J(t)$.

For long times, the elastic response and the delayed elasticity vanish, and thus

$$\eta=\tau_0/(\partial\gamma/\partial t), \tag{A2}$$

which defines the shear viscosity, η, for Newtonian fluids such as oxide glasses.

The change in time of some property of a glass, due to the imposed change of a variable (temperature, stress, etc.) can be calculated if one knows the viscoelastic functions—relaxation modulus $G(t)$ and the material compliance $J(t)$. An expression which relates $G(t)$ and $J(t)$ in the case of a constant shear stress τ_0 is given by

$$\tau_0=\gamma(0)G(t)+\int_0^t G(t-t')(\partial\gamma/\partial t')dt', \tag{A3}$$

where $\gamma(t)$ is given by Eq. (A1) which can be rewritten as

$$\gamma(t)=\tau_0 J(t), \tag{A4}$$

where $G(t)$ is the relaxation modulus $[G(t)=G_\infty\phi(t)$; and $\phi(t)$ is the shear relaxation function]; which normally has an exponential form. Expression (A3) is extensively used by rheologists and is discussed in several textbooks, e.g., Ref. 5. It is known as the *basic equation of linear viscoelasticity*.

From Eq. (A4), the shear strain rate is given by

$$\partial\gamma/\partial t=\tau_0\partial J/\partial t. \tag{A5}$$

Substituting (A4) and (A5) into (A3) one has

$$1=J(0)G(t)+\int_0^t G(t-t')\partial J/\partial t' dt'. \tag{A6}$$

This equation relates the viscoelastic functions; relaxation modulus $G(t)$, and compliance $J(t)$.

From Eq. (A1),

$$\partial J/\partial t=1/\eta+\partial h/\partial t. \tag{A7}$$

Substituting $J(0)=1/G_\infty$ and (A7) into Eq. (A6):

$$1=G(t)/G_\infty+\int_0^t G(t-t')[(1/\eta)+\partial h/\partial t']dt'. \tag{A8}$$

Thus

$$1=\phi(t)+(G_\infty/\eta)\int_0^t\phi(t-t')dt'+G_\infty\int_0^t\phi(t-t')$$
$$\times[\partial h/\partial t']dt'. \tag{A9}$$

In the limit $t\rightarrow\infty$, the first and third terms vanish, and therefore,

$$\eta=G_\infty\int_0^\infty\phi(t)dt. \tag{A10}$$

This is a rather extraordinary result, because the shear viscosity can be determined simply as an integral over time of the stress relaxation function $\phi(t)$.

Some insight can now be gained into *Eq. (1)*:

$$\eta=\langle\tau\rangle/C. \tag{A11}$$

Then a comparison of Eqs. (A10) and (A11) show that $C=1/G_\infty$ and

$$\langle\tau\rangle=\int_0^\infty\phi(t)dt, \tag{A12}$$

so $\langle\tau\rangle$ is the time average of the shear relaxation function!

2. The free-volume model of viscosity

Most elements and compounds when molten have a viscosity about the same as that of water (10^{-2} Pa s). On cooling the melt, crystallization occurs very rapidly a little below the freezing point T_f. There are, however, a few materials

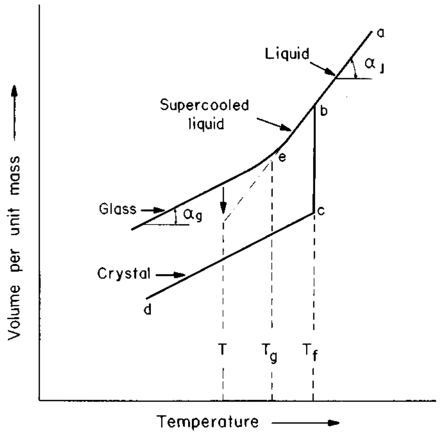

Fig. 3. Relation between the glassy, liquid, and solid states.

which form melts which are considerably more viscous. The high viscosity indicates that the atoms or molecules in the melt are not so easily moved relative to one another by applied stresses. On cooling below the freezing point, crystallization does occur, but at a significantly lower rate than in the materials of the first group. The process of crystallization involves structural changes, i.e., the rearrangement of atoms relative to one another. In simple terms, the relatively high viscosity of the melt and the low rate of crystallization are both consequences of the greater resistance to atomic rearrangement encountered in these materials.

If the crystallization rate is low enough, it is possible to go on cooling the melt below the freezing point without crystallization taking place. As the melt cools, its viscosity continues to increase. This viscous liquid below the freezing point is a *supercooled liquid*. Thus, strictly speaking, it is incorrect to refer to it as a glass. Further cooling results in the viscosity rising to such a high value that the mechanical properties of the material are closely similar to those of an ideal elastic solid. The viscosity will then be at least $10^{12}-10^{13}$ Pa s. This solid material is a glass.

The volume–temperature diagram shown in Fig. 3 is useful in discussing the transformation from a supercooled liquid to a glass. If the melt crystallizes on cooling, this is usually accompanied by a marked increase in density at the melting point, T_f. No such change occurs if the melt supercools. The volume decreases along the line *be*. The decrease in volume on cooling is due partly to the decreasing amplitude of atomic vibrations, and partly to changes in the structure of the melt which result in it becoming more compact as the temperature falls. At temperatures near T_f these structural changes can occur very rapidly and will appear to occur instantaneously following any change in the temperature of the material. As the viscosity increases with falling temperature, the structural changes occur increasingly slowly until eventually the viscosity becomes so high that no such further changes are possible in laboratory time scales. A decrease in slope is then found in the V vs T curve (point e). With a further fall of temperature, the decreasing volume is due almost entirely to the decreasing amplitude of the atomic vibrations.

The temperature at which the change in slope occurs is called the transformation temperature or glass transition temperature, T_g. Only below T_g is it correct to describe the material as a glass. The change from supercooled liquid to glass, which may be considered as taking place at this temperature, is not a sudden one, nor is T_g a well-defined temperature for any particular glass. Indeed the term ''transformation range'' is used more frequently than ''transformation temperature.'' The temperature at which the change in slope occurs is found to decrease as the rate of cooling is decreased. Also, if the glass is held at the temperature T, a little below T_g, its volume decreases slowly until it reaches a point on the dotted line, which is an extrapolation of the contraction curve of the supercooled liquid. The rate of change of volume decreases as the dotted line is approached, i.e., as the structure of the glass approaches an ''equilibrium'' configuration characteristic of the supercooled melt at the temperature T. This equilibrium configuration has a lower free energy than other liquidlike structures or configurations, but it is not, of course, that arrangement of molecules which has the lowest possible free energy at the temperature T (the crystalline arrangement). However, at temperatures significantly below T_g, the rate at which the liquidlike glass structure can change is inversely proportional to the viscosity and is very slow, as shown previously in this paper.

Cohen and Turnbull[10] developed a *free-volume* model of viscous flow based on the idea that flow occurs by movement of molecules (flow units) into voids of a size greater than some critical size. That is, the molecules rattle around in the cage created by surrounding molecules, until density fluctuations create a hole large enough for a molecule to jump into. The free volume (v_f) is somewhat vaguely defined, but it represents roughly the space not occupied by the core volume (v_0) of the molecules. The viscosity can be written as

$$\eta = \eta_0 \exp(\delta\, v_0/v_f), \tag{A13}$$

$$v_f/v_0 = \int_{T_0}^{T} (\alpha_1 - \alpha_g)\, dT', \tag{A14}$$

where δ is a constant close to unit, T_0 is the temperature where $v_f = 0$, and α_1 and α_g are the thermal expansion coefficients of supercooled liquid and glass, respectively ($\alpha_1 > \alpha_g$), shown in Fig. 3. This equation reduces to the VFT equation if $\alpha_1 - \alpha_g$ is constant.

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[1] Eduardo Mari, ''Los mitos del vidrio,'' Ceramica y Cristal **107**, 29 (1991).
[2] Michael Wysession, ''The inner workings of the earth,'' Am. Sci. **83**, 134–147 (1995).
[3] W. O. Fellers, *Materials Science, Testing and Properties* (Prentice-Hall, Englewood Cliffs, NJ, 1990), p. 204.
[4] *Encyclopedia Britannica*—''Viscosity'' (William Benton, Chicago, 1966), Vol. 23, p. 198.
[5] Steven Brawer, *Relaxation in Viscous Liquids and Glasses* (American Ceramic Society, Columbus, Ohio, 1985), p. 24.
[6] Narotan P. Bansal and Robert H. Doremus, *Handbook of Glass Properties* (Academic, Orlando, 1986).
[7] W. Muller, M. Torge, and K. Adam, ''Ratio of $CaO/K_2O > 2$ as an evidence of a special Rheinish type of mediaeval stained glass,'' Glastech. Ber.-Glass Science & Technology **67** (2), 45–48 (1994).
[8] T. Lakatos, L.-G. Johansson, and B. Simmingskold, ''Viscosity temperature relations in the glass system SiO_2-Al_2O_3-Na_2O-K_2O-CaO-MgO in the composition range of technical glasses,'' Glass Technology **13** (2), 88–95 (1972).
[9] Edgar D. Zanotto, ''Isothermal and Adiabatic Nucleation in Glass,'' J. Non-Cryst. Solids **89**, 361–370 (1987).
[10] David Turnbull and Morrel Cohen, ''On the free-volume model of the liquid-glass transition,'' J. Chem. Phys. **52** (6), 3038 (1970).