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Dynamics of Glass Relaxation at Room Temperature

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The problem of glass relaxation under ambient conditions has intrigued scientists and the general public for centuries, most notably in the legend of flowing cathedral glass windows. Here we report quantitative measurement of glass relaxation at room temperature. We find that Corning® Gorilla® Glass shows measurable and reproducible relaxation at room temperature. Remarkably, this relaxation follows a stretched exponential decay rather than simple exponential relaxation, and the value of the stretching exponent ($\beta = 3/7$) follows a theoretical prediction made by Phillips for homogeneous glasses.

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A common urban legend concerns the apparent flow of medieval stained glass windows, which are often found to be thicker at the bottom than at the top. Researchers have estimated that the viscosity of glass under ambient conditions is too high to yield any measurable flow on a human time scale, so these thickness variations are now rationalized as an artifact of medieval glass production techniques [1–3]. While this legend of glass flow has seemingly been put to rest, here we show a direct measurement of dimensional changes for an industrial silicate glass (Corning® Gorilla® Glass) at room temperature. These measurements reveal a total linear strain of ~10 ppm over the course of 1.5 yr of measurement. Remarkably, this relaxation follows a stretched exponential decay with a dimensionless stretching exponent of $\beta = 3/7$, corresponding to the value predicted by the Phillips diffusion-trap model for relaxation dominated by long-range pathways [4].

The relaxation behavior of glass is widely regarded as one of the most challenging unsolved problems in condensed matter physics [4,5]. The study of glass physics is made difficult owing to the three *non*s. Glass has a *noncrystalline*, liquidlike structure, lacking the intermediate and long-range periodicity found in crystalline solids. Furthermore, glass is a *nonequilibrium* material, continually relaxing toward the supercooled liquid state [6–9]. Thus, its properties depend on both its composition and its entire thermal and pressure histories. Finally, the glassy state is inherently *nonergodic*, since the relaxation time of a glass is typically much longer than directly accessible experimental time scales [8]. This is especially true for common silicate glasses at room temperature, where the relaxation times are considered to be much too long for direct observation on any reasonable human time scale [1–3]. Moreover, the magnitude of relaxation under such conditions is likely to be too small for precise detection using conventional techniques.

In this work, we overcome the problems of measurement precision by using a large (1050 × 1050 × 0.7 mm) sheet of Corning Gorilla Glass (code 2318), an aluminosilicate glass used as a chemically strengthened cover material for a variety of consumer electronics devices [10]. The glass is manufactured using the fusion draw process, which assures homogeneity of the glass sheet and yields pristine surface quality rivaled only by freshly drawn optical fiber [11]. A schematic diagram of our experimental setup is shown in Fig. 1. The surface of the unstrengthened glass sheet is scribed at 20 mm intervals along its width and length forming a series of intersections. An optical measurement is used to determine the positions of the intersections relative to corresponding marks on a reference plate in order to define the initial dimensions of the glass. The as-received glass is exposed to an initial 30-min heat treatment at 250 °C and then stored between measurements in a

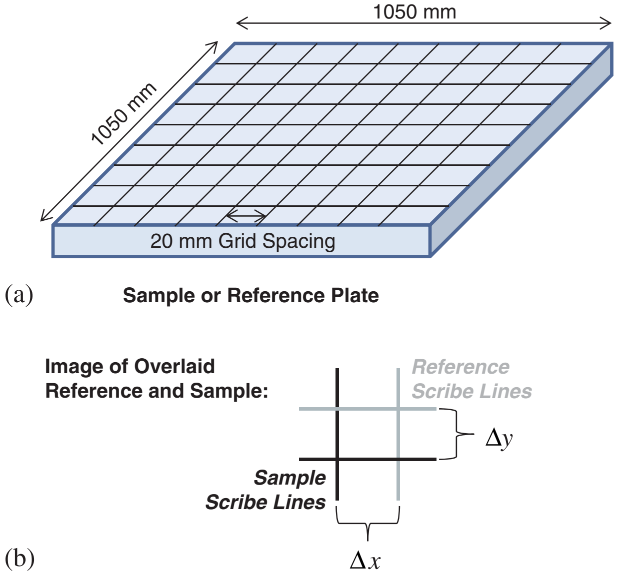

FIG. 1 (color online). Schematic diagram of the experimental setup for measuring strain as a function of relaxation time. (a) Grid of scribe lines marked on both the reference plate and the sample. (b) Image of overlaid grid lines from the reference and the sample, used to calculate the x and y displacements.

controlled temperature and humidity environment at 20 ± 0.1 °C, (50 ± 2)% relative humidity. After the first two months of measurements the samples were moved into a less tightly controlled environment at 20 ± 0.5 °C, with a humidity of (47 ± 5)% in the summer and (37 ± 5)% in the winter. The relaxation of the glass is monitored through repeated measurement of the scribed intersections on the glass sheet relative to the reference plate over a total experimental time of 1.5 yr. Owing to the large size of the glass sheet and the high precision of the optical measurement, the error of each individual strain measurement is about ±0.2 ppm. The magnitude of the error bar scales inversely with the linear dimensions of the glass sample, so if a more typically sized laboratory glass sample were to be used for this experiment, the errors bar would be significantly larger (e.g., an error of ±2.0 ppm for samples one-tenth the size of those used in our experiment).

Figure 2 shows the results of the relaxation experiment. Here the symbols represent individual linear strain measurements for two separate samples over time t, and the solid blue line represents a fit of the strain data using a stretched exponential decay function, $\exp[-(t/\tau)^{\beta}]$, with a dimensionless stretching exponent of $\beta = 3/7$, which according to Phillips diffusion-trap theory is the characteristic value of β for relaxation dominated by long-range pathways [4]. The fitted value of the relaxation time is $\tau = 27.6$ d. A separately fitted simple exponential decay curve, corresponding to $\beta = 1$, is also plotted for comparison. Figure 2 reveals several interesting features of the glass relaxation behavior. First, the initial 30-min, 250 °C heat treatment of the glass produces a net room temperature expansion of the glass of ~3 ppm, indicating the presence of a relaxation mode that becomes excited at temperatures significantly lower than the glass transition temperature, T_g, of the glass ($T_g = 620\,^{\circ}\mathrm{C}$ for Gorilla Glass). The second and most surprising feature is that the glass measurably relaxes at room temperature, a result that defies the conventional wisdom that the relaxation time of a high-T_g silicate glass is much too long to observe relaxation at room temperature conditions [1–3]. Third, during the full 1.5-yr duration of the experiment, the glass compacts by ~10 ppm, leading to a final linear strain of about −7 ppm. This result indicates than even without the initial 30-min, 250 °C heat treatment there are low-temperature excited modes in the as-formed glass. While here we report a quantitatively precise room temperature relaxation curve for an industrial silicate glass, such low temperature relaxation has also been observed qualitatively in the so-called thermometer effect [12,13], discovered in the 1890s as a shift in the zero point of glass thermometers as they aged.

The observed relaxation is apparently unrelated to the viscous flow of the bulk glass, which is depicted in Fig. 3. The viscosity measurements were conducted according to the procedures described by Mauro *et al.* [14,15]. Equilibrium viscosity measurements were performed using

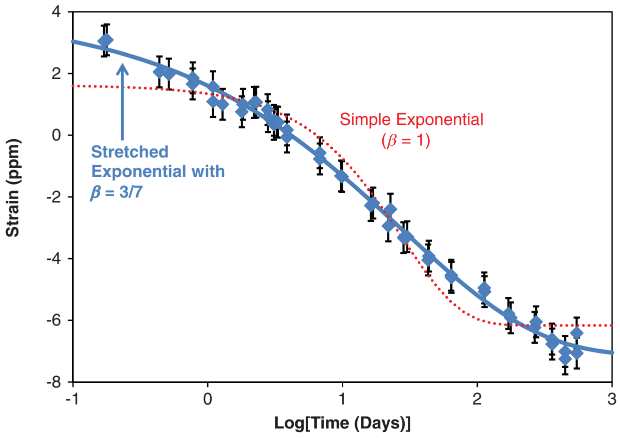

FIG. 2 (color online). Room temperature relaxation of two 1050 × 1050 × 0.7 mm sheets of Corning® Gorilla® Glass (code 2318) after being quenched from an initial 30-min heat treatment at 250 °C. The symbols show the individual linear strain measurements over a total experimental time of 1.5 yr. Throughout the course of the experiment the glass sheets were stored in controlled temperature and humidity environments as described in the text. The solid blue line shows a fit of this strain data using a stretched exponential decay function with an exponent of $\beta = 3/7$, which is characteristic of relaxation dominated by long-range pathways. The fitted value of the relaxation time is $\tau = 27.6$ d. A separately fitted simple exponential decay curve is also shown for comparison.

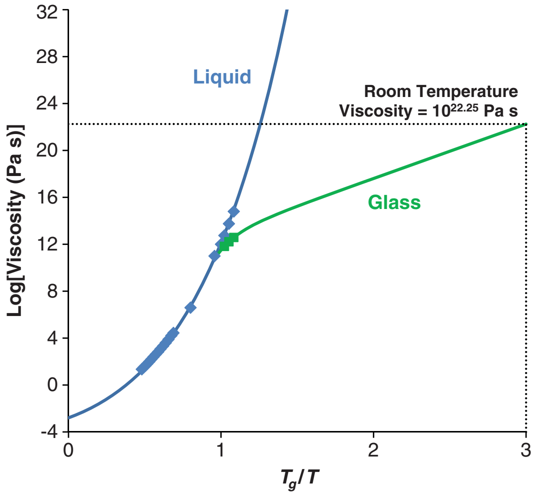

FIG. 3 (color online). Viscosity of Corning Gorilla Glass in the equilibrium (liquid) and nonequilibrium (glassy) regimes. Viscosity measurements were performed according to the procedures described in the text and in Refs. [14,15]. The liquid- and glassy-state viscosity data are fit using the MYEGA [14] and MAP [15] models, respectively. Extrapolation of the nonequilibrium glassy viscosity curve to room temperature gives an estimated viscosity of $10^{22.25}$ Pa s, which corresponds to a structural relaxation time on the order of 19 000 yr. Thus, the room temperature relaxation shown in Fig. 2 is not a product of viscous flow.

a concentric cylinder method at high temperature and parallel plate viscometry at the softening point ($10^{6.6}$ Pa s). Lower temperature equilibrium and nonequilibrium viscosity measurements were conducted using beam bending viscometry at temperatures as low as 550 °C. Beam bending viscometry measurements were performed as a function of time to capture the relaxation of the viscosity curve from the nonequilibrium glassy state to the equilibrium supercooled liquid state. The measured viscosity data are fit using the MYEGA [14] and MAP [15] expressions in the equilibrium and nonequilibrium regimes, respectively, and lead to an estimated room temperature glassy-state viscosity of $\sim 10^{22.25}$ Pa s. When this value of viscosity is divided by the shear modulus of the glass (29.5 GPa) following Maxwell's relation, an estimated structural relaxation time on the order of 19 000 yr is obtained. This relaxation time associated with viscous flow is, of course, much too long to explain any dimensional changes of the glass on a time scale of only 1.5 yr.

Figure 2 also shows the surprising result that the relaxation curve can be accurately modeled using a stretched exponential decay function, $\exp[-(t/\tau)^{\beta}]$, rather than a simple exponential decay as predicted by two-state models [16,17]. The stretched exponential function was proposed empirically over 150 years ago by Kohlrausch [18] for its functional simplicity and accuracy in describing relaxation data. The stretched exponential function contains just two free parameters: the relaxation time τ and the dimensionless stretching exponent β, which satisfies $0 < \beta \leq 1$. The upper limit of $\beta = 1$ corresponds to simple exponential decay, while lower values of β are indicative of a more complicated nonexponential relaxation process, giving rise to a "fat tail" [19]. Of all such distributions with fat tails, the stretched exponential has been shown to provide the best description of the relaxation behavior of homogeneous glassy systems [4].

A major breakthrough in understanding the physical origin of stretched exponential relaxation can be found in the 1982 work of Grassberger and Procaccia [20], which was subsequently extended by Phillips [4,21–24] in the so-called "diffusion-trap" model. This model considers a uniform distribution of excitations that diffuse to sinks or traps, which annihilate the excitations. Those excitations located closest to the traps are annihilated first, while those farther away take longer to disappear, and stretched exponential relaxation is obtained [4]. In this model, the stretching exponent is derived as $\beta = d^*/(d^* + 2)$, where d^* is the effective dimensionality of the channels along which the excitations relax. This can be expressed as $d^* = fd$, where d is the dimensionality of the system ($d = 3$ for structural glasses) and f is the fraction of channels activated for the particular relaxation process. In the simple case of $d = 3$ with all channels activated ($f = 1$), a stretching exponent of $\beta = 3/5$ is derived [4]. Based on an assumption of equipartitioning of the relaxation channels into short- and long-range contributions ($f = 1/2$), a fractal dimensionality of $d^* = 3/2$ is obtained for the long-range relaxation pathways. With this fractal value, one obtains a stretching exponent of $\beta = d^*/(d^* + 2) = 3/7$ for relaxation governed by long-range interactions. This theory represents an important advance since previously β was considered to be an empirical fitting parameter [25] with little or no underlying physical significance. Recently, this model has also been shown to have surprising implications outside the traditional realm of physics [26,27].

In order to assess the validity of the 3/7 exponent based on the available data in Fig. 2, we ran Monte Carlo simulations using 20 000 pairs of samples incorporating the ±0.2 ppm error bar on each measurement and assuming measurements at the same time points as in the experiment. On this basis the 90% confidence interval for β from our data set lies in the range [0.36, 0.44]. This rules out other exponents such as 1/2 or 3/5 but confirms the likelihood of $3/7 \approx 0.43$.

We attribute the ability of Corning Gorilla Glass (code 2318) to relax at room temperature to the presence of mixed alkali ions in the glass network, a phenomenon that is also attributed as the source of the thermometer effect [12,13]. To confirm this notion of mixed alkali ions as the source of room temperature dynamics, we have also performed similar measurements as in this study for several fusion-drawn alkali-free aluminosilicate glasses [11] as well as the more recent single alkali-containing Gorilla Glass 2 (code 2319) and Gorilla Glass 3 (code 2320) compositions, but no discernable relaxation was observed for any of these glasses at room temperature.

The fact that the dynamics of room temperature relaxation in code 2318 Gorilla Glass are stretched exponential in nature is expected for a glass satisfying the criteria of homogeneously distributed excitations and traps, i.e., excited and ground state locations for the alkali ions. Our results also indicate that stretched exponential relaxation is intrinsic in microscopically homogeneous disordered systems, regardless of whether the relaxation is connected to viscous flow. The particular value of the exponent ($\beta = 3/7$) observed in our experiment provides a direct indication of the physical origin of this parameter, with structural relaxation pathways dominated by long-range interactions.

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